An aerial photograph of a large offshore oil rig, primarily orange and white, situated in the middle of a blue ocean. The rig has multiple levels and complex structures. A prominent feature is a large discharge pipe extending from the rig down into the water, with a thick plume of white water being discharged. The rig is supported by several vertical legs. In the background, another similar rig is visible. The sky is not clearly visible, suggesting a high-angle shot.

Composition, Environmental Fates, and Biological Effect of Water Based Drilling Muds and Cuttings Discharged to the Marine Environment:

A Synthesis and Annotated Bibliography

Submitted to
PERF

Prepared by
Jerry M. Neff

January 2005

Battelle
The Business of Innovation

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Prepared for

**Petroleum Environmental Research Forum (PERF)
and
American Petroleum Institute**

Prepared by

**Jerry M. Neff
Battelle
Duxbury, MA**

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ABSTRACT

Water based drilling muds (WBM) consist of fresh or salt water containing a weighting agent (usually barite: BaSO₄), clay or organic polymers, and various inorganic salts, inert solids, and organic additives to modify the physical properties of the mud so that it functions optimally. Drill cuttings are particles of crushed rock produced by the grinding action of the drill bit as it penetrates the earth.

The U.S. Environmental Protection Agency, or a state environmental agency designated by EPA, regulates discharges of drilling muds and cuttings to state and federal waters of the U.S. Current National Pollutant Discharge Elimination System (NPDES) permits allow discharge of WBM and cuttings to federal, but not state, waters if they meet restrictions in the Effluent Limitation Guidelines (ELG).

WBM are pumped from the mud tanks on the platform down the hollow drill pipe and exit the drill string through holes in the drill bit. They sweep cuttings from the drill bit up the space between the drill string and the wall of the well (the annulus) to the platform deck. The mud/cuttings mixture is passed through separation equipment that separates the cuttings from the drilling mud, which is returned to the mud tanks for recirculation down-hole. If permitted by local regulations, the cuttings may be discharged to the ocean. Periodically, some of the drilling mud may be discharged as well. The total mass of WBM and cuttings discharged per exploratory well is about 2000 metric tons/well, and somewhat less for most development wells.

When WBM and cuttings are discharged to the ocean, the larger particles and flocculated solids, representing about 90 % of the mass of the mud solids, form a plume that settles quickly to the bottom. The remaining 10 % of the mass of the mud solids consisting of fine-grained unflocculated clay-sized particles and a portion of the soluble components of the mud form another plume in the upper water column that drifts with prevailing currents away from the platform and is diluted rapidly in the receiving waters. In well-mixed ocean waters, drilling muds and cuttings are diluted by 100-fold within 10 m of the discharge and by 1000-fold after a transport time of about 10 minutes at a distance of about 100 m from the platform. Because of the rapid dilution of the drilling mud and cuttings plume in the water column, harm to communities of water column plants and animals is unlikely and has never been demonstrated.

WBM and cuttings solids settle to and accumulate on the sea floor. If discharged at or near the sea surface, the mud and cuttings disperse in the water column over a wide area and settle as a thin layer of a large area of the sea floor. If mud and cuttings are shunted to and discharged just above the sea floor in order to protect nearby sensitive marine habitats, the drilling solids may accumulate in a large, deep pile near the discharge pipe.

The accumulation of mud and cuttings on the bottom, the cuttings pile, may contain higher concentrations of several metals, particularly barium (from drilling mud barite), and sometimes petroleum hydrocarbons than nearby uncontaminated sediments. Chromium, lead, and zinc are the metals, in addition to barium, that are most often enriched in cuttings pile sediments. Until EPA placed limits on the concentrations of cadmium and mercury concentration in drilling mud barite in 1993, some of the barite used in drilling muds contained elevated concentrations (compared to concentrations in natural marine sediments) of several metals. Cuttings piles containing these muds often contained elevated concentrations of several metals.

Barite has a very low solubility in sea water. The metals associated with drilling mud barite are present as insoluble sulfide minerals. Several laboratory and field studies have shown that the metals associated with drilling mud barite or cuttings piles have a low bioavailability to marine animals; they do not accumulate in the tissues of bottom-living animals.

Small amounts of petroleum products may be added to WBM for lubrication or they may be associated with the cuttings drilled during penetration of some geologic formations. These hydrocarbons may accumulate in the cuttings pile. Although WBM containing petroleum hydrocarbons are more toxic than those without any hydrocarbons, WBM cuttings piles usually do not contain sufficient petroleum hydrocarbons to harm bottom-living communities. Petroleum hydrocarbon concentrations greater than about 50 to 60 mg/kg in cuttings piles often are associated with altered benthic community diversity. These concentrations usually are not observed unless synthetic base mud cuttings or oil based mud cuttings were discharged.

WBM are non-toxic or practically non-toxic to marine animals, unless they contain elevated concentrations of petroleum hydrocarbons, particularly diesel fuel. Most drilling mud ingredients are non-toxic or used in such small amounts in WBM that they do not contribute to its toxicity. Chrome and ferrocchrome lignosulfonates are the most toxic of the major WBM ingredients. Although used frequently in the past in the Gulf of Mexico, these defloculants are being replaced in most WBM by non-toxic alternatives to reduce the ecological risk of drilling discharges.

Many field monitoring studies, mostly in the U.S. Gulf of Mexico and the North Sea, have been performed since the 1970s to determine short- and long-term impacts of drilling discharges on the marine environment. As a general rule, effects of WBM and cuttings discharges on the bottom environment are related to the total mass of drilling solids discharged and the relative energy of the water column and benthic boundary layer at the discharge site. In high energy environments, little drilling waste accumulates on the sea floor and adverse effects of the discharges can not be detected. In low-energy environments or where mud and cuttings are shunted to near the sea floor, large amounts of mud and cuttings solids may accumulate on the sea floor and adversely affect bottom communities within a few hundred m of the discharge.

Effects of WBM cuttings piles on bottom living biological communities are caused mainly by burial and low sediment oxygen concentrations caused by organic enrichment. Toxic effects, when they occur, probably are caused by sulfide and ammonia byproducts of organic enrichment. Recovery of benthic communities from burial and organic enrichment occurs by recruitment of new colonists from planktonic larvae and immigration from adjacent undisturbed sediments. Ecological recovery usually begins shortly after completion of drilling and often is well advanced within a year. Full recovery may be delayed until concentrations of biodegradable organic matter decrease through microbial biodegradation to the point where surface layers of sediment are oxygenated.

Use of the Annotated Bibliography

The attached CD contains extended abstracts of more than 200 publications and reports dealing with the environmental fates and effects of water based drilling muds. Most of the citations in the text of the synthesis are included in the annotated bibliography. The complete text of the synthesis is also included on the CD. The CD is in Adobe format and can be searched by author or subject. The CD can also be used as a subject index for the review paper.

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1.0 INTRODUCTION

1.1 Offshore Exploration and Development

Exploration for and development and production of offshore oil and gas resources is a massive, long-term undertaking that may cause physical, chemical, and biological disturbance to the local marine environment. Offshore oil and gas operations can be divided into two phases: exploration and development/production. Development and production may occur together at large offshore facilities.

Drilling of wells is the main activity in exploration and development. Exploratory drilling involves drilling wells to determine if fossil fuels (oil and gas) are present (OGP, 2003). If fossil fuels are discovered during exploratory drilling, additional appraisal and delineation wells may be drilled to determine the size and economic potential of the fossil fuel reservoir. If commercial quantities of oil or gas are identified, the operator may drill several development wells to produce the fossil fuels.

Exploration, appraisal, and development drilling are essentially the same, though the facilities from which drilling occurs often are different. Most exploratory drilling is performed from jackup rigs (to about 150 m water depth) or anchored or dynamically-positioned semi-submersible rigs (to more than 3,500 m water depth). Development drilling and production usually are performed from large fixed or floating platforms. Subsea completions are becoming more common, particularly in deep water. These differences affect the options available for drilling mud and cuttings management (Veldman and Lagers, 1997; CAPP, 2001; OGP, 2003).

Development drilling is a much more massive undertaking than exploratory drilling and, therefore, has a greater potential to affect the local marine environment. Drilling of offshore production wells may take place from fixed or floating platforms, or occasionally from artificial islands. From 10 to 50 and occasionally up to 100 wells may be drilled from each platform. One or two wells can be drilled at a time from a platform, and each well may require a few weeks to six months to drill. Full development of a field may involve one or several platforms, up to several hundred wells, and may take a few to as many as twenty years. Production may continue for twenty years or more. During production, maintenance drilling is required periodically. In development of a large field, the usual practice is to bring wells into production as they are drilled. Thus, drilling and oil and gas production go on simultaneously from an offshore platform during much of the life of an offshore field.

1.2 Definitions of Water Based Drilling Muds and Cuttings

Historically, most oil and gas wells drilled since about 1900 have been drilled by the rotary drilling process (Allen, 1981). The Lucas gusher at Spindletop, Texas, was drilled in 1901 with a rotary drill and drilling fluid consisting of water, finely ground cuttings from the hole, and clays from local surface soils. Drilling is accomplished by a rotating drill bit attached to the end of a hollow drill pipe, referred to as the drill string (Figure 1). A fluid is pumped down the drill pipe, exits through holes in the drill bit, and returns to the surface in the annulus, the space between the drill pipe and the wall of the drilled hole. Rotation of the drill bit at the bottom of the hole breaks off small chips of rock, deepening the hole. The fluid exiting the drill bit suspends these rock chips, called cuttings, and carries them up the annulus to the surface where they are removed from the fluid and disposed of. The fluid, the drilling mud, usually is recycled down-hole.

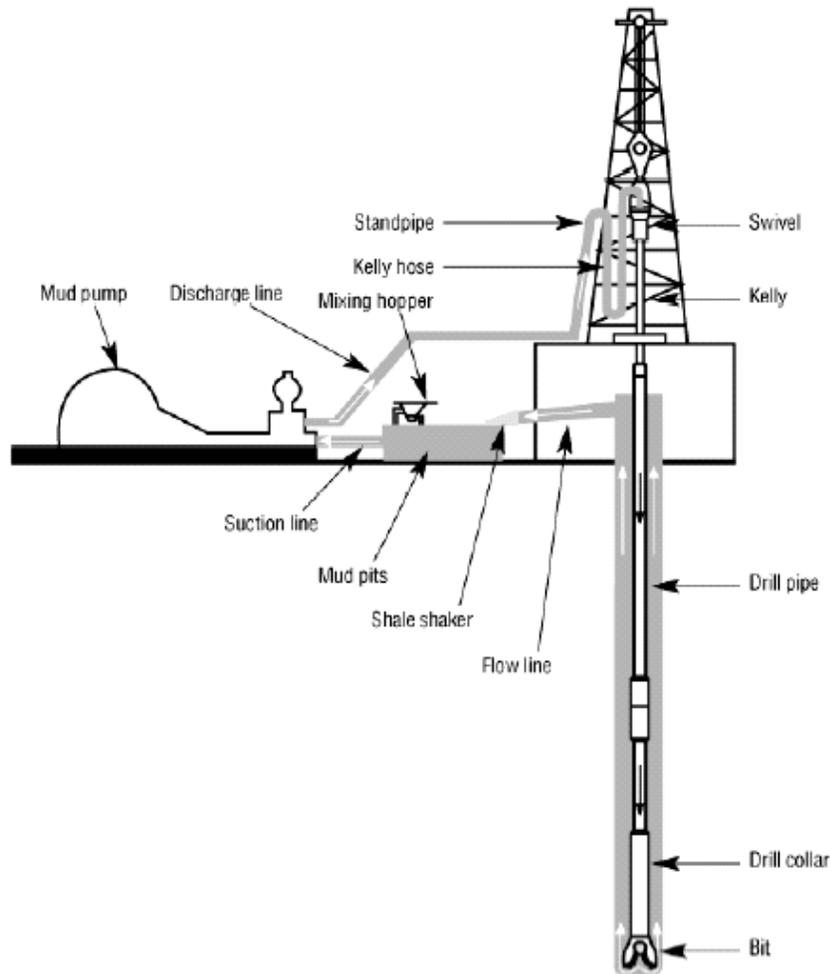


Figure 1. Drilling circuit on an offshore platform. The drilling mud is pumped from the mud pit through the Kelley and down the center of the drill pipe. It exits through the drill bit, where it picks up drill cuttings and lubricates the drill bit. It passes up the annulus (the space between the drill string and the borehole wall) to the mud return line, through the shale shake and other mud/cuttings separation devices, and back to the mud pit. See Figure 3 for pictures of components of the mud/cuttings separation devices. From CAPP (2001).

A wide variety of fluids has been used for rotary drilling, including water, or a mud-in-water slurry, oil, synthetic organic fluids, brine-in-oil or synthetic emulsions, mists, and foams (Whittaker, 1985; OGP, 2003). Most modern drilling muds are mixtures of fine-grained solids, inorganic salts, and organic compounds in water or an organic liquid. There are two primary types of drilling muds (also called drilling fluids) in use today: water based drilling muds (WBM), and non-aqueous drilling muds (NADM) (Neff et al., 2000; OGP, 2003). WBM, used in most offshore drilling operations in US waters, consist of fresh or salt water containing barite, clay or an organic polymer, and various inorganic salts and organic additives to modify the physical properties of the mud. In NADM, the continuous phase is a mineral oil or synthetic hydrocarbon, usually emulsified with a brine, and containing barite, organophilic clays or polymers, and various additives.

1.3 Functions of Water Based Drilling Muds

The earliest drilling muds were slurries of mud (silt and clay) in water. They didn't work well, particularly as drilling depths increased. A variety of ingredients was added to allow the drilling mud to function efficiently under a variety of down-hole conditions. Modern drilling muds have several functions critical to the rotary drilling process. They include (Neff et al., 1987; OGP, 2003):

- Counteracting formation pressure. The column of drilling mud in the drill pipe and annulus provides a hydraulic head (weight) that counteracts the pressure in the formations being drilled, preventing formation fluids from flooding the well bore, causing a blowout.
- Removing cuttings from the borehole. Jets of drilling mud exiting from the drill bit carry drill cuttings away from the bit, preventing it from clogging, and convey them to the surface.
- Suspending solids. The drilling mud must have sufficient viscosity to suspend cuttings and weighting agent when drilling stops, as during addition of new lengths of drill pipe. This function is particularly important during drilling of horizontal wells.
- Cooling and lubricating the drill string and bit. Friction of the rotating drill string heats the drill pipe and, particularly the bit. Circulating drilling mud cools the drill string and lubricates it where contact is made with the formation, at the drill bit, and in curved sections of deviated or horizontal wells.
- Protecting, supporting, and stabilizing the borehole wall. Some types of formation minerals, particularly shales, are sensitive to water and swell and slough off the side walls into the well bore during drilling, decreasing wellbore quality. WBM may contain additives to minimize shale swelling.
- Protecting permeable zones from damage. Special drilling mud additives build a filter cake (a low-permeability layer of packed solids) on the walls of the well, preventing drilling mud loss into permeable formations, which may damage the formation and increase drilling costs.
- Supporting part of the weight of the drill string. The steel drill pipe is supported in the hole in proportion to the volume and density of the drilling mud displaced by the pipe in the annulus.

1.4 Objectives of Literature Review and Annotated Bibliography

The wastes generated in the largest volumes during exploration and development drilling are drilling muds and cuttings. In many parts of the world, some types of drilling muds and drill cuttings may be discharged to the ocean if they meet certain environmental requirements. The objective of this review and annotated bibliography is to summarize our current knowledge about the fates in the ocean and ecological effects of WBM and drill cuttings discharged from offshore platforms. The review is a brief synthesis and integration of the research and monitoring performed on WBM from the early 1970s to 2004. The annotated bibliography includes brief summaries on the most important publications on the environmental behavior and effects of WBM, with focus on publications since 1983, the date of the National Research Council (1983) publication on: "Drilling Discharges in the Marine Environment." A similar review and annotated bibliography is available for synthetic based drilling muds (SBM) and SBM cuttings (Neff et al., 2000).

1.5 Topics of the Review

The review is organized in logical fashion, proceeding from WBM and cuttings composition to ecological effects of and recovery from drilling mud and cuttings discharges to the ocean. The review starts with a discussion of the composition of different types of WBM, with a description of the characteristics of the most commonly used major ingredients and additives in WBM. There also is a description of the physical and chemical properties of drill cuttings.

WBM and cuttings management varies in different parts of the world because of differences in usage patterns and environmental regulations. Current U.S. environmental regulations for drilling mud and

cuttings discharges are summarized. We describe the drilling mud handling system typical of offshore platforms, separation of cuttings from drilling muds, and discharge practices for processed mud and cuttings. The rates and volumes of drilling mud and cuttings discharged also are discussed.

We then discuss the environmental fate of WBM and cuttings that are discharged from offshore platforms. The effect of environmental factors and mud and cuttings properties on their environmental fates are discussed. Measured and modeled dispersion of mud and cuttings particles and accumulation of waste solids on the bottom are discussed.

The ingredients of major environmental concern in WBM and cuttings are several metals and petroleum hydrocarbons. We discuss the bioavailability and toxicity of these drilling mud ingredients in relation to their physical and chemical form in drilling wastes. Physical effects (burial and changes in water column turbidity and sediment properties) of drilling waste discharges on marine ecosystems also are discussed. Finally, the review contains a summary of the results of field studies on the ecological effects of and recovery from ocean discharge of WBM and cuttings.

2.0 COMPOSITION OF WATER BASED DRILLING MUDS (WBM) AND DRILL CUTTINGS

2.1 Drilling Muds Used Offshore in the U.S. and Abroad

Three types of drilling muds are used offshore (Neff et al., 2000). They include water based drilling muds (WBM), and two types of non-aqueous drilling muds (NADM), oil based drilling muds (OBM), and synthetic based drilling muds (SBM), sometimes called pseudo-oil based drilling muds (PBM). In WBM, the liquid or continuous phase is fresh water or seawater (National Research Council, 1983; Neff et al., 1987).

The earliest drilling muds were WBM, and were composed mainly of clay (mud) and a weighting agent. Because they did not perform well under some down-hole conditions, a variety of chemicals were added to the basic WBM formula to solve different down-hole problems. Refined oil, usually as diesel fuel, which is used on offshore rigs for running electric generators and other machinery, often was added to lubricate the drill string or to help free stuck pipe. The oil in WBM helped stabilize the wellbore wall, leading to the development of OBM to drill in difficult shale formations. OBM were widely adopted for upland drilling and for offshore drilling in the North Sea, Canada, and several other offshore production areas. Used OBM usually were not discharged, but were returned to shore for reprocessing or disposal. However, OBM cuttings usually were discharged to the ocean. OBM and OBM cuttings never were permitted by EPA for ocean discharge to U.S. territorial waters, limiting the use of OBM for offshore drilling in the US. The US EPA has always required that OBM used offshore and associated cuttings be returned to shore for reprocessing or upland disposal.

Experience in the North Sea revealed that diesel OBM cuttings were highly toxic and persistent in marine sediments (cuttings piles) near platforms (Davies et al., 1983; Kingston, 1987; Olsgard and Gray, 1995). Diesel was replaced in OBM by low-aromatic mineral oils in an effort to reduce harmful environmental impacts. Mineral oil OBM cuttings also were harmful to bottom-living biological communities near platforms and OBM were gradually replaced by SBM in which the continuous phase is a low-toxicity, biodegradable, synthetic organic compound, usually an olefin or ester (Neff et al., 2000). SBM cuttings usually are permitted for offshore disposal to U.S. Federal waters, and at offshore drilling sites elsewhere. Monitoring and assessment programs are being performed in several offshore development areas in the world to determine if SBM cuttings provide significant environmental advantages over OBM cuttings (Neff et al., 2000; Continental Shelf Associates, 2004). Because of concerns over the discharge of SBM and OBM cuttings enriched in organic matter, there is an ongoing interest in improving technical and environmental properties of WBM so that they can be used to drill difficult offshore formations and be discharged to the ocean or land with minimal long-term environmental harm.

2.2 Water Based Drilling Muds (WBM)

WBM is a suspension of particulate minerals, dissolved salts, and organic compounds in freshwater, seawater, or concentrated brine. WBM ingredients can be divided into 18 functional categories (National Research Council, 1983; World Oil, 1999):

- Weighting materials
- Viscosifiers
- Thinners, dispersants
- Alkalinity, pH-control additives
- Bactericides
- Filtrate reducers
- Flocculants
- Foaming agents
- Lost circulation materials
- Pipe-freeing agents

- Calcium reducers
- Corrosion inhibitors
- Defoamers
- Emulsifiers
- Shale control inhibitors
- Surface-active agents
- Temperature stability agents
- Lubricants

Each functional group of additives may contain several alternative materials with slightly different properties (Table 1). Although more than 1,000 trade name or generic additives are available for drilling mud formulation, most WBM contain no more than about 20 additives, most are added in small amounts to change mud properties to solve specific down-hole problems. The most abundant ingredients (other than water) in most WBM are barite weighting material, salts (in several functional categories), and bentonite viscosifier (Figure 2).

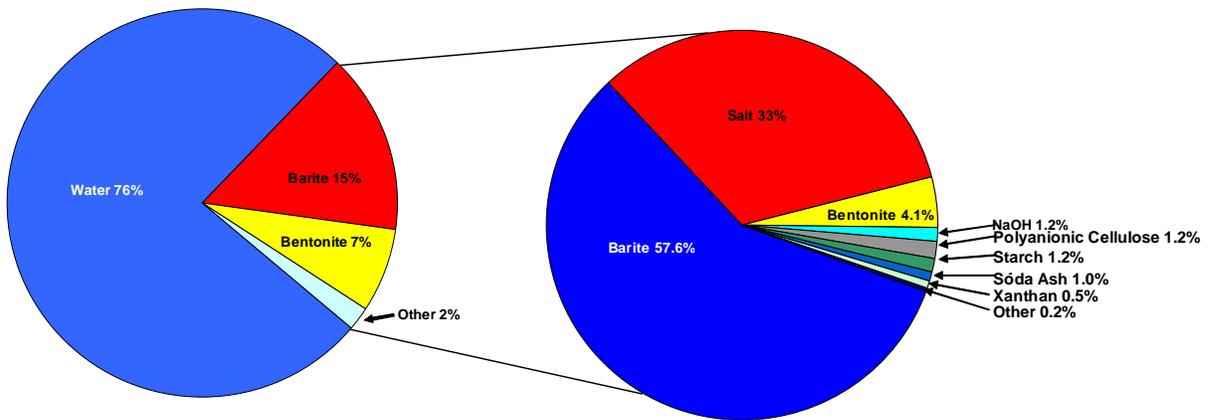


Figure 2. Composition of a typical water based drilling mud (WBM) and of the additives to a typical WBM.

Table 1. Functional categories of materials used in WBM, their functions, and examples of typical chemicals in each category. From Boehm et al. (2001).

Functional Category	Function	Typical Chemicals
Weighting Materials	Increase density (weight) of mud, balancing formation pressure, preventing a blowout	Barite, hematite, calcite, ilmenite
Viscosifiers	Increase viscosity of mud to suspend cuttings and weighting agent in mud	Bentonite or attapulgite clay, carboxymethyl cellulose, & other polymers
Thinners, dispersants, & temperature stability agents	Deflocculate clays to optimize viscosity and gel strength of mud	Tannins, polyphosphates, lignite, ligrosulfonates
Flocculants	Increase viscosity and gel strength of clays or clarify or de-water low-solids muds	Inorganic salts, hydrated lime, gypsum, sodium carbonate and bicarbonate, sodium tetraphosphate, acrylamide-based polymers
Filtrate reducers	Decrease fluid loss to the formation through the filter cake on the wellbore wall	Bentonite clay, lignite, Na-carboxymethyl cellulose, polyacrylate, pregelatinized starch
Alkalinity, pH control additives	Optimize pH and alkalinity of mud, controlling mud properties	Lime (CaO), caustic soda (NaOH), soda ash (Na ₂ CO ₃), sodium bicarbonate (NaHCO ₃), & other acids and bases
Lost circulation materials	Plug leaks in the wellbore wall, preventing loss of whole drilling mud to the formation	Nut shells, natural fibrous materials, inorganic solids, and other inert insoluble solids
Lubricants	Reduce torque and drag on the drill string	Oils, synthetic liquids, graphite, surfactants, glycols, glycerin
Shale control materials	Control hydration of shales that causes swelling and dispersion of shale, collapsing the wellbore wall	Soluble calcium and potassium salts, other inorganic salts, and organics such as glycols
Emulsifiers & surfactants	Facilitate formation of stable dispersion of insoluble liquids in water phase of mud	Anionic, cationic, or nonionic detergents, soaps, organic acids, and water-based detergents
Bactericides	Prevent biodegradation of organic additives	Glutaraldehyde and other aldehydes
Defoamers	Reduce mud foaming	Alcohols, silicones, aluminum stearate (C ₅₄ H ₁₀₅ AlO ₆), alkyl phosphates
Pipe-freeing agents	Prevent pipe from sticking to wellbore wall or free stuck pipe	Detergents, soaps, oils, surfactants

Table 1. Functional categories of materials used in WBM, their functions, and examples of typical chemicals in each category. From Boehm et al. (2001).

Functional Category	Function	Typical Chemicals
Calcium reducers	Counteract effects of calcium from seawater, cement, formation anhydrites, and gypsum on mud properties	Sodium carbonate and bicarbonate (Na_2CO_3 & NaHCO_3), sodium hydroxide (NaOH), polyphosphates
Corrosion inhibitors	Prevent corrosion of drill string by formation acids and acid gases	Amines, phosphates, specialty mixtures
Temperature stability agents	Increase stability of mud dispersions, emulsions and rheological properties at high temperatures	Acrylic or sulfonated polymers or copolymers, lignite, lignosulfonate, tannins

2.2.1 Weighting Materials.

Barite (barium sulfate: BaSO_4) is a soft, dense ($4.1 - 4.5 \text{ g/cm}^3$) natural mineral used as a weighting agent in drilling muds of all types (National Research Council, 1983; Neff et al., 2000). Drilling mud barite used offshore in the US must be least 92 weight % pure, have a specific gravity greater than 4.2 g/cm^3 , and 97 weight % must pass through a $75\text{-}\mu\text{m}$ screen, with no more than 30 % smaller than $6 \mu\text{m}$ in diameter (API, 1993). Mineral impurities in barite include silica, iron oxide, limestone, and dolomite, as well as several metals, mostly in the form of metal sulfides (Table 2). Low trace metal barite is available in the U.S. for drilling muds used and discharged offshore.

Table 2. Concentrations of selected metals in Battle Mountain (Utah), high purity barite (BaSO_4). From Nelson et al. (1984). Concentrations are mg/kg (ppm).

Element	Concentration	Element	Concentration
Barium	503,000	Potassium	350
Iron	1,600	Chromium	599
Sodium	2,920	Copper	6
Zinc	7	Arsenic	1
Calcium	610	Cadmium	0.2
Lead	1	Nickel	3.8
Magnesium	280	Mercury	0.2

Hematite (iron oxide: Fe_2O_3) occasionally is used instead of barite to prepare a high-density WBM or OBM for use in deep drilling (Ch. Hard, 1984). It is a red powder with a density of 5.3 g/cm^3 . Mineral impurities in hematite include quartz, rutile, and pyrite.

OSPAR (2004) has included ilmenite (iron titanium oxide: FeTiO_3) on the PLONAR list (substances used and discharged offshore which are considered to pose little or no risk to the environment) to encourage its use as a replacement for barite in drilling muds discharged to the North Sea, because of concern about possible environmental impacts of metals sometimes found in barite. Ilmenite has a density of 4.5 to 5.0 g/cm^3 and may contain a wide variety of mineral impurities, including zircon, hematite,

magnetite, rutile, and spinel. Ilmenite usually contains lower concentrations of metals than barite does. Hematite and ilmenite apparently are not used in U.S. offshore WBM.

Large amounts of barite are used in drilling muds, particularly when drilling deep wells or penetrating geopressured strata. The amount of barite added to drilling mud generally increases from about 2.2 lb/barrel (6.3 kg/m³) near the surface to as much as 700 lb/barrel (2,000 kg/m³) near the bottom of a deep well (National Research Council, 1983). A barrel is a volumetric measure used by the oil industry and is equivalent to 42 gallons or 0.159 m³. It is possible, by use of barite, to produce a water based drilling mud weighing up to about 2,276 kg/m³, more than twice the density of water (Hudgins, 1991). This weight is used to counteract the pressure of the formation being drilled, preventing a blowout.

The average amount of barite in drilling muds used to drill wells offshore in the U.S. Gulf of Mexico increases with well depth from about 61,200 lbs for wells up to 5,000 ft deep to more than 800,000 lbs for wells greater than 10,000 ft deep (Boehm et al., 2001). More barite is required in drilling muds for deep-water wells, ranging from 3 to 10 million lbs for wells in 1000ft to more than 4000 ft of water. The total amount of barite used in the Gulf of Mexico in 1998 to drill 559 shallow-water wells was 326 million lbs and to drill 43 deep-water wells was 272 million lbs (1.23x10⁵ metric tons) (Table 3).

Table 3. Masses of solid and volumes of liquid drilling mud ingredients discharged to the Gulf of Mexico from offshore drilling operations in 1998. Shallow-water wells were drilled in less than 1000 ft of water. From Boehm et al. (2001).

Functional Category	Shallow-Water Wells	Deep-Water Wells
Total number of wells	559	43
Weighting Materials (lbs)	326,000,000	372,000,000
Viscosifiers (lbs)	46,500,000	13,200,000
Thinners, dispersants, & temperature stability agents (lbs)	8,850,000	4,960,000
Filtrate reducers (solid & liquid) (lbs)	7,700,000	5,543,000
Alkalinity, pH control additives & calcium reducers (lbs)	13,200,000	4,620,000
Lost circulation materials (lbs)	11,700,000	5,380,000
Lubricants (gal)	183,000	---
Shale control materials (liquids) (gal)	1,210,000	763,000
Shale control materials (solids) (lbs)	6.660,000	14,000,000
Emulsifiers & surfactants (gal)	150,000	1,700
Bactericides (gal)	850	---
Defoamers (gal)	17,000	123,000
Scale inhibitors (gal)	584	---
Total solids (lbs)	420,000,000	419,000,000
Total liquids (gal)	1,560,000	890,000

2.2.2 Viscosifiers.

Bentonite clay (sodium montmorillonite), or sometimes attapulgite clay, usually is the second most abundant ingredient in most WBM (Figure 2). Clay is added to drilling mud to maintain the gel strength required to suspend and carry drill cuttings to the surface. Bentonite forms a thixotropic gel in the well bore. The shear from the rotation of the drill string and bit liquefy the bentonite slurry, facilitating mud pumping. When drilling stops, the bentonite gels, preventing suspended cuttings and barite from settling

out, clogging the annulus. Several WBM additives are used to optimize these rheological properties of the clay. Bentonite also helps to coat the wall of the borehole to prevent loss of fluids (water and dissolved mud ingredients) to permeable formations.

Frequently, the clay is replaced, all or in part, by cellulose polymers and starch when drilling a soft formation, such as shale. The polymers maintain the viscosity of the mud better than clays do, without damaging the soft formation. Carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC) are prepared from plant cellulose (Hudgins, 1991). They usually are reacted with sodium hydroxide to produce soluble sodium salts. These cellulose polymers are added to drilling muds to aid in control of fluid loss to the formation and to increase the viscosity of the drilling mud.

Starch, starch derivatives and guar gum are polysaccharide polymers derived from plants. Xanthan gum, derived from bacterial degradation of carbohydrates may be used at concentrations of 0.6 to 6 kg/m³ in WBM. These water-soluble polymers are used primarily to increase the viscosity and solids carrying capacity of the drilling mud (Hudgins, 1991). They often supplement or replace bentonite in drilling muds in low-temperature drilling applications. Drilling muds containing these polymers usually are treated with biocides to inhibit microbial degradation of the polysaccharides. The biocide used most frequently for this purpose is glutaraldehyde, which degrades rapidly and is not persistent in the environment.

Between 13,000 and 100,000 lbs of clay and/or 350 to 700 lbs of polymers are used as viscosifiers in drilling muds used to drill a well in shallow-water in the Gulf of Mexico (Boehm et al., 2001). Larger amounts, up to 300,000 lbs of clay and 13,000 lbs of polymer may be used in deep-water drilling muds. The total amounts of clay and polymers used as viscosifiers in all drilling muds use in the Gulf of Mexico in 1998 were 59 million lbs and 739,000 lbs, respectively (Table 3). If some of the drilling is through clay formations, the drilling mud may become contaminated with formation clay, necessitating dilution of the mud with water and frequent replacement of the mud. Thus, the total amounts of clays that may be released to the environment during drilling of a well may be quite large. Drilling mud clays are not considered toxic, but may contain elevated concentrations of several metals, mostly tightly bound to the clay matrix (National Research Council, 1983).

2.2.3 Thinners and Dispersants.

As well depth increases, it is necessary to add more weighting agent to the drilling mud to counteract down-hole pressure. More bentonite has to be added to support the added weight of the barite and lift it and the cuttings out of the hole. Addition of barite and bentonite to the mud increases its viscosity, increasing the pressure needed to pump it, increasing the risk of loss of water and drilling solids to the formation. Various thinners or dispersants are added to bentonite WBM to decrease viscosity, improving pumpability. They usually act by complexing with the charged surfaces of clay platelets, preventing flocculation. The early thinners, such as sodium chloride and inorganic polyphosphates were effective only in freshwater muds. Quebracho bark was used in the 1940s and 50s, but was sensitive to high formation temperatures. Lignosulfonates, lignites, and tannins were introduced in the 1950s and for many years have been the most frequently used thinners for offshore bentonite-based WBM. Cellulose polymer muds, even those containing some bentonite, usually do not contain much lignosulfonate and lignite.

Lignosulfonates are organic polymers derived from the lignin of wood and are byproducts of the pulp and paper industry (Hudgins, 1991). When complexed with certain inorganic ions, such as chromium, iron, or calcium, at an alkaline pH, they are effective in preventing flocculation of clays. Sodium hydroxide (NaOH) is added to lignosulfonate WBMs to maintain a pH of about 10; lignosulfonates are most effective as deflocculents at alkaline pH. Although lignosulfonates are water-soluble, they react strongly with bentonite, becoming part of the insoluble bentonite platelets (Hudgins, 1991). Lignosulfonates also are good emulsifiers and aid in control of fluid loss to the formation (filtration control).

Chrome and ferrochrome lignosulfonates are the most effective mud thinners. The chrome in chrome- and ferrochrome-lignosulfonates is present in the less toxic, insoluble trivalent state (CrIII), and is tightly bound to the lignosulfonate. If a chrome lignosulfonate drilling mud is used in a high-temperature formation, it may be necessary to add inorganic chromate salts (CrVI) to the mud to prevent thermal destruction of the lignosulfonate. The added chromate oxidizes the lignosulfonate and in the process is reduced to less soluble and toxic chromic (CrIII) salts. Chrome lignosulfonates, often including added chromate, are considered the most toxic components of most water-based drilling muds that do not contain added petroleum (Conklin et al., 1983). Therefore, the U.S. and North Sea oil industries usually replace chrome lignosulfonates with iron or calcium lignosulfonates or other deflocculents in drilling muds destined for ocean disposal.

Lignite (a soft brown coal), applied as a fine powder, is used with lignosulfonates as a clay deflocculation and filtration control agent. An oxidized lignite, called leonardite, composed primarily of degraded humic acids, is used most frequently in WBM (Hudgins, 1991). Humic acids have a low aqueous solubility and help to control fluid loss to the formation. Lignite may be converted under alkaline conditions to sodium or potassium lignite salts that are water-soluble; these are the lignite derivatives that are used with lignosulfonates as deflocculents and filtration control agents. In clay muds containing both lignosulfonates and lignite, the amounts used are approximately equal.

The total amount of lignosulfonate, lignite, and other thinners used in drilling muds for a single well in the Gulf of Mexico ranges from about 3×10^3 lbs to 1.45×10^5 lbs ($1400 - 6.58 \times 10^4$ kg). The total mass discharged to the Gulf of Mexico in 1998 was about 13.8×10^6 lbs (6.26×10^6 kg) (Table 3).

2.2.4 Other Drilling Mud Additives.

A wide variety of other additives is available for changing the physical/chemical properties of a drilling mud so that it will function optimally during drilling of a well (Ranney, 1979; Hudgins, 1991, 1994) (Tables 1 and 3). A wider variety of additives is used in WBM than in OBM or SBM. Most are used in small amounts and are not considered toxic.

Sulfonated salts of asphalt or gilsonite (a natural asphaltic material) may be added in small amounts to WBM for control of fluid loss to permeable formations. Asphalt is derived from the residual fraction produced by refining crude oil. Asphalts are composed mainly of resins and asphaltenes, high molecular weight saturated and aromatic hydrocarbon polymers.

Lubricants, including diesel fuel and vegetable or mineral oils, may be added to WBM to reduce torque and drag on the drill string, particularly when drilling a deviated well. They usually are added at concentrations between 5,000 and 150,000 mg/L and are not added continuously during drilling. Occasionally, the drill pipe becomes stuck in the hole. In order to free the pipe, the mud engineer may add a slug or pill of an OBM and pump it into the area where the pipe is stuck. The OBM pill may contain more than 600,000 mg/L of a diesel or mineral oil (Neff et al., 1987). After the stuck pipe is freed, the OBM pill may be recovered and separated from the WBM system and disposed of on land. In the past, the OBM pill, which usually represents only a small fraction of the total mass of the mud in use, sometimes was allowed to mix completely with the WBM.

Most of the toxicity of WBM containing diesel or mineral oil is caused by the oil (Conklin et al., 1983; Gaetz et al., 1986; Breteler et al., 1988; Ayers et al., 1989). Therefore, the U.S. EPA (1993, 1996) has banned the discharge to the ocean of drilling muds containing free oil, so offshore use of OBM and diesel and mineral oil additives to WBM have declined. When an OBM is required to solve a particular down-hole problem, the OBM and cuttings are recovered and sent to shore for onshore disposal.

Water-soluble emulsifiers may be added to WBM containing hydrocarbon lubricants to disperse the oil in the water phase of the mud (Hudgins, 1991). They include fatty acids, sulfonates, and polyoxylates, some of which may contribute to the toxicity of the drilling mud. Alkylphenol polyethoxylates (APEO) were used in the past as emulsifiers in North Sea drilling muds. However, the octylphenol and nonylphenol degradation products are endocrine-disruptor toxicants and, for this reason, these emulsifiers have been replaced with less toxic products for drilling and production offshore in the North Sea (Getliff and James, 1996).

Hydrogen sulfide may seep into the well bore from the formation or it may be produced by degradation of drilling mud chemicals. Hydrogen sulfide is highly corrosive to drilling equipment and is a health risk to platform personnel. Under the alkaline conditions of most drilling muds, nearly all the sulfide is present as the dissolved bisulfide ion (HS^-). However, carbon dioxide may accompany the sulfide from the formation, reducing the pH of the mud. The usual method for removing sulfide from drilling mud is with inorganic sulfide scavengers. These scavengers react with both H_2S and HS^- to produce insoluble metal sulfide salts. The most frequently used sulfide scavengers in drilling muds are iron oxides, zinc oxide, and basic zinc carbonates. These metal salts react with sulfides to form insoluble iron sulfide (FeS_2) and zinc sulfide (ZnS), respectively.

2.2.5 Metals.

Several metals are present in most WBMs (Table 4). The metals of greatest concern, because of their potential toxicity and/or abundance in drilling fluids, include arsenic, barium, chromium, cadmium, copper, iron, lead, mercury, nickel, and zinc (Neff et al., 1987, 2000). Some of these metals are added intentionally to drilling muds as metal salts or organo-metallic compounds. Others are present as trace impurities in major mud ingredients, particularly barite and clay.

Table 4. Concentration ranges of several metals in WBM from different sources and in typical soils and marine sediments. Concentrations are mg/kg dry wt (ppm). Modified from Neff et al. (1987). Metals that sometimes are present in drilling muds at concentrations more than 10 times those in natural sediments are shaded in bold.

Metal	Drilling Muds ¹	Clay-Loam Soils ²	Sediments ³
Barium	720 – 449,000	150 – 1,500	1 – 2,000
Chromium	0.1 – 5960	20 – 100	36 – 110
Cadmium	0.16 – 54.4	0.01 – 7	0.1 – 0.6
Copper	0.05 – 307	7 – 70	7 – 33
Iron	0.002 – 27,000	---	20,000 – 60,000
Mercury	0.017 – 10.4	<0.01 – 0.90	0.03 – 0.14
Lead	0.4 – 4226	<10 – 70	10 – 33
Zinc	0.06 – 12,270	20 – 220	27 – 88
Nickel	3.8 – 19.9	5 – 50	13 – 45
Arsenic	1.8 – 2.3	1.7 – 27	6.9 – 26
Vanadium	14 – 28	---	63 – 238
Aluminum	10,800	---	10,000 – 90,000
Manganese	290 – 400	50 – 2,000	100 – 10,000

¹ From Neff (1982); ² from Breckenridge and Crockett (1995); ³ from Robertson and Carpenter (1976); Siegel et al. (2000); Neff (2002a).

The metals most frequently present in drilling muds at concentrations substantially (>100-fold) greater than natural concentrations in soils and sediments are barium, chromium, lead, and zinc (Table 4). Mercury sometimes was present at elevated concentrations in US, Canadian, and North Sea drilling muds; it was derived from mercury contamination of drilling mud barite (Neff, 2002b). The U.S. EPA (1993) placed restrictions on the maximum amount of mercury in drilling mud barite destined for ocean disposal in 1993. With wider use of low-trace-metal barite for muds, average mercury concentrations in US WBM have declined, though concentrations usually still are higher than background concentrations in clean marine sediments.

The most abundant metal in most WBM is barium (actually an alkaline earth element like calcium and strontium). Nearly all the barium in drilling mud is from barite (BaSO_4) added to the mud to increase its density. Clays and clay-rich shales may contain high concentrations of barium. Natural marine sediments and the cuttings themselves also contain barium; barium concentration in sediments tends to be inversely related to sediment grain size. Clean, fine-grained marine sediments may contain more than 1,000 mg/kg barium. Most of the barium in sediments is in barite. Barite in drilling muds and sediments has a low solubility in seawater, because of the high natural concentration of sulfate in the ocean. Because it is insoluble in seawater, it has a low bioavailability and toxicity to marine organisms.

When present at elevated concentrations, compared to concentrations in clean sediment, drilling mud chromium is derived primarily from chrome- or ferrochrome-lignosulfonates or chromate salts added intentionally to the mud for viscosity control. Barite and bentonite clay may also contain traces of chromium (Table 2). The chromium in a used drilling mud, even that added as chromate, is in the trivalent, chromic valency state. Trivalent chromium salts have low solubilities and limited mobility in the environment. They usually have a low toxicity to plants and animals.

Most of the other metals sometimes detected in drilling muds are present primarily as trace impurities in barite, clay, or the drill cuttings in the formation penetrated by the drill bit. The most abundant metals in barite are barium (not a true metal), lead, zinc, and iron (Table 5); some barites also may contain elevated concentrations of chromium (Table 2). Commercial barites contain micro-inclusions of barium feldspar, galena (lead sulfide), pyrite (iron sulfide), sphalerite (zinc sulfide), quartz, and silicates (Ansari et al., 2001); it is probable that the metals are present in barite primarily associated with insoluble sulfide salts (Kramer et al., 1980; Leutermaier et al., 1997; Trefry, 1998; Trefry and Smith, 2003). These metal sulfides have an extremely low solubility and mobility, even in anoxic, sulfidic sediments where some of the barite dissolves (Trefry, 1998; Shimmield and Breuer, 2000; Trefry and Smith, 2003).

Table 5. Mean concentrations of metals in samples of a low trace metal barite similar to that currently used for offshore drilling muds in the U.S (Trefry et al., 1986) and in barites used for drilling muds in the Norwegian Sector of the North Sea in 2001 (Schaanning et al., 2002). Concentrations are $\mu\text{g/g}$ dry wt (ppm).

Metal	U.S. Barite	Norwegian Barite
Arsenic	2.2	2.0
Cadmium	0.03	0.7
Chromium	11	13.1
Copper	9.7	76.6
Iron	10,100	24,800
Lead	7.8	54.5
Mercury	0.12	0.31
Nickel	NA	1.2
Zinc	8.6	42.9

NA not analyzed.

Lead, zinc, and copper also may enter drilling mud in pipe thread compound (pipe dope) or drill collar dope used to lubricate the threads and promote electrical conduction between pipe sections (Ayers et al., 1980). The dopes contain several percent metallic metal; some of the dope gets into the drilling mud, contaminating it. As mentioned above, various zinc salts may be added intentionally to drilling mud for control of hydrogen sulfide.

2.3 Oil Based Drilling Muds (OBM) and Synthetic Based Drilling Muds (SBM)

It is helpful to understand the physical and chemical properties of oil based drilling muds (OBM) and synthetic based drilling muds (SBM) to better understand why they differ from WBM in environmental behavior and ecological effects.

2.3.1 Oil Based Drilling Muds.

OBM are similar to WBM, except that the continuous phase is a refined petroleum product rather than water. OBM have many operational advantages over WBM, particularly WBM in which additives have been eliminated because of environmental concerns (Bloys et al., 1994). OBM provide excellent wellbore stability in difficult reactive shale formations, good lubricity, temperature stability, a reduced potential for differential sticking of the drill string, and low formation damage. They are particularly effective for drilling deviated or long-reach wells. Because of these advantages and the characteristics of the geologic formations being drilled, OBM were the preferred muds for drilling in the North Sea until discharge of OBM cuttings was restricted and ultimately banned. OBM, because of their toxicity and cost, usually are not discharged to the ocean. OBM and SBM usually are returned to shore where they are reprocessed and recycled, to the extent possible by current technology, for use in drilling new wells. OBM cuttings have been discharged offshore to the North Sea, the Canadian continental shelf, and offshore waters in many other parts of the world. Such discharges to the North Sea were phased out in the early 1990s. Where WBM are not suitable and reinjection or upland disposal of OBM cuttings is cost prohibitive, OBM have been replaced by SBM; cuttings containing small amounts of SBM solids are permitted for ocean discharge in many parts of the world, including Federal waters (> 3 miles from shore) of the Gulf of Mexico.

2.3.2 Synthetic Based Drilling Muds.

In an effort to develop drilling muds that are more environmentally acceptable than OBM, with the technical advantages of OBM, the oil industry developed a group of SBM (Candler et al., 1993; Bloys et al., 1994; Veil et al., 1996). The base fluids of synthetic-based muds, as the name suggests, are composed of well-characterized chemical compounds synthesized specifically for formulation of the mud product (Neff et al., 2000). In SBM, the continuous phase is a synthetic organic ester, ether, acetyl, or olefin. Most SBM used today in the Gulf of Mexico are linear- α -olefins, internal olefins, or esters (Table 6). Some SBM formulations contain a mixture of 2 or 3 synthetic organic chemicals, usually olefins and esters.

The concentration of the synthetic organic phase of a SBM is similar to that of refined oil in an OBM, about 30 to 90 percent of the total volume of the mud; the synthetic chemical usually represents about 20 to 40 percent of the mass of the mud (Kenny, 1993).

OBM and SBM also often contain barite, clays, emulsifiers, water, calcium chloride, lignite, and lime. Water or a saline brine (usually containing calcium chloride: CaCl_2), at a concentration of 10 to 50 volume percent, is dispersed into the hydrocarbon phase to form a water-in-organic phase emulsion with water droplets less than 1 μm in diameter (Hudgins, 1991; Norwegian Oil Industry Association Working Group, 1996). This emulsion is stable because of the small size of the water droplets and because

emulsifiers often are used to stabilize it. It is called an invert emulsion because water is dispersed in the organic phase and formation solids that come in contact with the drilling mud become oil-wet.

Table 6. Names and chemical structures of synthetic chemicals used most frequently in the Gulf of Mexico for SBM. From Neff et al. (2000).

Synthetic Chemical Type	Generic Chemical Structure
Linear- α -Olefin (LAO)	$\text{CH}_3 - (\text{CH}_2)_n - \text{CH} = \text{CH}_2$
Internal Olefin (IO)	$\text{CH}_3 - (\text{CH}_2)_m - \text{CH} = \text{CH} - (\text{CH}_2)_n - \text{CH}_3$
Ester	$\begin{array}{c} \text{CH}_3 - (\text{CH}_2)_n - \text{C} = \text{O} \\ \quad \quad \quad \backslash \\ \quad \quad \quad \text{O} - (\text{CH}_2)_m - \text{CH}_3 \end{array}$

Emulsifiers, which usually are heavy metal soaps of fatty acids, are added to the muds at concentrations of 5 to 14 g/L to aid in oil/water emulsification (Ch. Hard, 1984). Wetting agents are added to ensure that the solids in the mud are oil-wet. Wetting agents include polyamines, fatty acids, and oxidized tall oils. An organophilic clay that is compatible with the oil or synthetic polymer phase of the mud is used instead of native bentonite; it is produced by treating bentonite clay with a quaternary amine. Lignite or lignosulfonate may be added to prevent flocculation of the clay. Soluble salts, usually of calcium, are added to prevent shale hydration. Lime is added to make calcium soaps that aid in emulsifying the water in the oil.

SBM are more biodegradable and less toxic than most OBM, while retaining many of the technical advantages of OBM (Neff et al., 2000). Because of their high cost, SBM usually are recycled rather than disposed of in the environment or reinjected. However, some SBM reaches the ocean in drill cuttings discharges, where these are permitted. Cleaned SBM cuttings usually contain about 10 percent synthetic chemical (Annis, 1997; Neff et al., 2000). Cuttings cleaning technology is being developed that can reduce the concentration of synthetic on cuttings to below 5 percent. Cuttings containing less than about 5 percent synthetic do not clump when discharged to the ocean; they disperse and settle over a wide area, preventing development of a cuttings pile and speeding biodegradation (Getliff et al., 1997). The new general NPDES permit for the western Gulf of Mexico, introduced in February 2002, requires that retention of synthetic base chemical on cuttings not exceed 6.9% (for internal olefins) or 9.4% (for esters) (Rabke et al., 2003).

2.4 Drill Cuttings

2.4.1 Mineralogy of Cuttings.

Drill cuttings are particles of crushed rock produced by the grinding action of the drill bit as it penetrates into the earth (Neff et al., 1987). Drill cuttings range in size from clay-sized particles ($\sim 2 \mu\text{m}$) to coarse gravel ($> 30 \text{ mm}$) and have an angular configuration. Their chemistry and mineralogy reflect that of the sedimentary strata being penetrated by the drill. The solids control (shale shaker) discharge (mainly drill cuttings) from an exploratory rig on the Mid-Atlantic outer continental shelf contained 21 % montmorillonite, 11 % each of illite and chlorite (all three are clays), and 22 % quartz, with smaller amounts of dolomite and siderite (iron carbonate) (EG&G, Environmental Consultants, 1982). Cuttings from wells drilled in the North Sea typically are composed primarily of sandstone and shale (Gerrard et al., 1999). Westerlund et al. (2001) identified quartz and barite as the two most abundant minerals in cuttings from the Beryl A and Ekofisk 2/4A platforms. The quartz probably is from the sandstone in the cuttings and the barite is primarily from the drilling mud solids adhering to the cuttings. Pyrite (iron sulfide) also is abundant. Illite and kaolinite are the dominant clay minerals present in North Sea drill

cuttings and may have come, in part, from the drilling mud solids adhering to the cuttings particles. These also are the dominant clays in continental shelf sediments of the North Atlantic (Griffin et al., 1968).

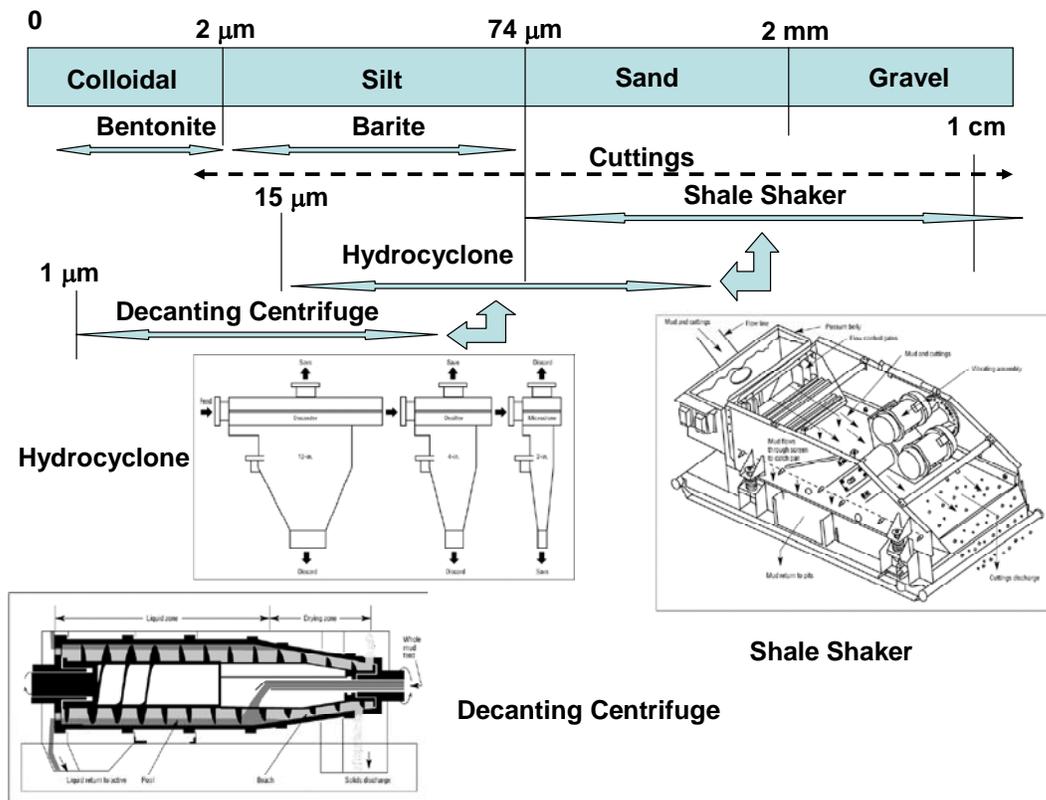


Figure 3. Separation of WBM and cuttings is mainly based on particle size and relies on shale shakers, hydrocyclones, and occasionally a decanting centrifuge. Most cuttings are sand/gravel-sized and are easily recovered on the shale shaker. However, silt- and clay-sized cuttings are difficult to separate from the barite and bentonite of WBM; hydrocyclones and centrifuges may be required.

2.4.2 Mud/Cuttings Separation.

Drilling muds containing cuttings are circulated through several separation devices on the platform to separate the drill cuttings particles from the drilling mud, which is recirculated down the hole (Figure 3) (National Research Council, 1983; Neff et al., 1987). The coarser, sand/gravel-sized cuttings particles are removed by the shale shakers. The solids that pass through the shale shaker screens may be passed to hydrocyclones and, occasionally, decanting centrifuges, where finer particles are removed. However, hydrocyclones and decanting centrifuges are not efficient in selectively removing cuttings solids from bentonite-based WBM, because the target cuttings for these devices are in the size range of the barite and clay fractions of the WBM. The solids control system on a platform usually removes more 75 percent of the cuttings from a WBM, unless the cuttings are composed mainly of silt-clay sized particles (CAPP, 2001). The remaining 25 percent, mostly clay-sized particles, tends to increase the viscosity of the mud.

Frequently, when drilling a clay-rich formation, mud viscosity is controlled by dilution (addition of make-up water) of the return from the shale shaker to maintain an optimum bentonite concentration and viscosity. This WBM management strategy requires frequent bulk discharges of drilling mud.

2.4.3 Chemical Composition of Drill Cuttings.

Drill cuttings contain, in addition to formation solids, small amounts of liquid and solid drilling mud components. The amounts of drilling fluid solids that remain attached to cuttings vary, depending on the grain size of the crushed rock from the strata being drilled. Clay sized cuttings are more difficult than larger cuttings to separate from drilling mud. A typical cuttings discharge during drilling with WBM usually contains 5 to 25 percent drilling fluid solids after passage through the solids control equipment on the platform. Cuttings from the fossil fuel-bearing intervals in a well also may contain crude oil or gas condensate.

The chemical composition of drill cuttings reflects the geochemistry of the formation being drilled and the amount of drilling mud ingredients adhering to the cuttings at the time of disposal. For example, the metals concentrations in drill cuttings discharged to offshore waters of California are similar to those of the drilling muds used to drill the wells (Table 7). Barium is more abundant in drilling mud than cuttings, as expected because of its abundance in drilling muds. Lead in one sample and zinc in both samples are more abundant in cuttings than in the drilling muds, indicating high concentrations in the formation rocks being drilled, or contamination of the cuttings with pipe thread compound. Most of the metals associated with cuttings are in immobile forms in minerals from the geologic formations.

Table 7. Concentrations of several metals in WBM and drill cuttings from two offshore platforms in southern California. Concentrations are mg/kg dry wt (ppm). From Phillips et al. (1998).

Metal	Platform 1		Platform 2	
	Drilling Mud	Cuttings	Drilling Mud	Cuttings
Barium	53,900	15,084	12,500	1180
Silver	0.37	0.50	0.39	0.63
Arsenic	10	10	9.3	13
Cadmium	1.17	2.89	1.75	3.62
Chromium	91	104	84	94
Copper	24	70	24	56
Mercury	0.09	0.07	0.06	0.04
Nickel	39	47	42	17
Lead	23	356	40	32
Vanadium	76	100	46	---
Zinc	167	664	235	972

Cuttings produced during drilling with WBM may contain small amounts of petroleum hydrocarbons. The hydrocarbons in cuttings generated with WBM may come from spotting fluids and lubricants added to the mud, or from the geologic strata being penetrated by the drill. Drilling mud and cuttings from all depths in a well off California contained petroleum hydrocarbons (Table 8). At all depths the drilling muds contained higher concentrations of total petroleum hydrocarbons and lower concentrations of total and individual PAH than the cuttings, suggesting that the PAH were derived primarily from the formations being drilled.

Table 8. Concentrations of hydrocarbons in composite samples of WBM and drill cuttings (in parentheses) from three drilling depths in a well on a platform in the Point Arguello Field, California. Concentrations are $\mu\text{g/g}$ dry wt (ppm). From Steinhauer et al. (1994).

Chemical	Surface	Mid-well	Bottom	Average
Total Petroleum Hydrocarbons ¹	159 (600)	137 (95)	988 (526)	390 (407)
Total PAH ²	0.87 (2.3)	8.0 (12)	51 (121)	25 (45)
Naphthalenes ³	0.27 (1.2)	5.4 (8.9)	39 (96)	18 (35)
Fluorenes ³	ND (ND)	0.38 (0.35)	4.1 (8.2)	2.8
Phenanthrenes ³	0.34 (0.79)	0.94 (0.64)	4.5 (9.3)	2.8 (3.6)
Dibenzothiophenes ³	0.03 (ND)	0.71 (0.40)	3.9 (8.1)	1.9 (2.8)

¹ Total resolved + unresolved hydrocarbons. ² Total 2- through 5-Ringed PAHs plus alkyl homologues. ³ Includes parent PAH and alkyl homologues.

The source of the high TPH in the cuttings from near the surface is unknown. Total and individual PAH concentrations increased with depth in the well. TPH and PAHs in the cuttings from the bottom of the well closely resembled the crude oil in the reservoir and probably were from the hydrocarbon-bearing formation.

3.0 Fates of WBM and Cuttings Discharged To the Ocean

3.1 Regulation of Drilling Discharges

Discharges to the ocean of WBM and cuttings are regulated in the US by the Federal Water Pollution Control Act (commonly known as the Clean Water Act). The Environmental Protection Agency (EPA) or a state environmental agency designated by EPA administers provisions of this act that apply to oil and gas activities in State and Federal waters.

There are three options for disposal of wastes generated offshore during exploration, development, and production of oil and gas resources:

1. Discharge to the ocean
2. Underground injection
3. Haul to shore for upland disposal or recycling.

EPA has the responsibility under the Clean Water Act to regulate discharges to the ocean. Upland disposal is under the jurisdiction of EPA and State environmental agencies.

Sections 402 and 403 of the Clean Water Act require that National Pollutant Discharge Elimination System (NPDES) permits for discharges to the territorial seas, the contiguous zone, and the ocean be issued in compliance with EPA's regulations for preventing unreasonable degradation of the receiving waters (U.S. EPA, 1993, 1996). Before a permit can be issued, the discharge must be evaluated in relation to EPA's published criteria for determination of unreasonable degradation. EPA develops effluent limitations guidelines (ELG) and new source performance standards (NSPS) that are intended to protect the receiving water environment from unreasonable degradation. Discharges of wastes from offshore platforms to the ocean must comply with ELG and NSPS in NPDES permits.

EPA develops these ELG and NSPS based on the degree of control that can be achieved using various levels of pollution control technology. In establishing ELG, EPA must consider the technologies that are already successfully in use, costs and economic impacts of implementation of the control technologies, and non-water quality environmental impacts of the discharge or alternative treatment technologies or disposal options.

Most discharges of wastes to Federal waters from offshore platforms are covered by general NPDES permits issued by the responsible EPA regions or State environmental agencies authorized by EPA. General permits cover all offshore platform discharges within a designated area, such as the western Gulf of Mexico. EPA also can issue a special NPDES permit for a single facility if it determines that geological, environmental, or cultural conditions or requirements at the site warrant specific, usually more stringent, permit conditions. The following EPA regions are responsible for issuing NPDES permits for discharges from offshore oil and gas rigs and platforms:

- EPA region 4 – Eastern Gulf of Mexico outer continental shelf (waters off Mississippi, Alabama, and west Florida);
- EPA Region 6 – State and Federal waters of the central and western Gulf of Mexico (waters off Texas and Louisiana);
- EPA Region 9 – outer continental shelf waters off California; and
- EPA Region 10 – State and Federal waters of Alaska (Cook Inlet and Beaufort Sea).

The current ELG for discharges of WBM, OBM, SMB and associated cuttings are summarized in Table 9. WBM and associated cuttings are no longer permitted for discharge to State waters (within 3

miles of land). Discharge of WBM and associated cuttings is permitted in Federal waters (> 3 miles from shore) if they meet permit requirements (Table 9). Discharge of WBM or cuttings containing refined, mineral, or formation (crude) oil is forbidden. The discharge of OBM and associated cuttings has never been permitted in US State or Federal waters.

SBM are not permitted for discharge to US State or Federal waters. They are recovered and recycled for use in drilling additional wells. However, drill cuttings generated during drilling with SBM are permitted for discharge to Federal, but not to State waters of the Gulf of Mexico and Cook Inlet, AK, if they meet certain requirements (Table 9). The new General Permit (CAG280000) for Federal waters off southern California, scheduled to become effective on 1 December, 2004, prohibits discharge of both SBM and SBM cuttings. As with WBM, formation oil and diesel fuel oil must be absent from the cuttings as indicated by a static sheen test.

Table 9. Current Effluent Limitation Guidelines (ELG) for discharges of drilling muds and cuttings to State and Federal waters of the United States from offshore oil and gas exploration and development platforms.

Waste Source and Receptor Body	Pollutant Parameter	Effluent Limitation
WBM and cuttings - Discharge to State waters ^a	All	No discharge
WBM and cuttings - Discharge to Federal waters ^c	Suspended particulate phase toxicity	Minimum 96-h LC ₅₀ ^b of suspended particulate phase of 3% by volume to the mysid <i>Mysidopsis bahia</i>
	Free oil	No discharge
	Diesel fuel oil	No discharge
	Mercury	Maximum 1 mg/kg dw in stock barite
	Cadmium	Maximum 3 mg/kg dw in stock barite
OBM and cuttings - Discharge to State or Federal Waters	All	No discharge
SBM - Discharge to State or Federal waters	All	No discharge
Drill cuttings associated with SBM - Discharge to State waters	All	No discharge
Drill cuttings associated with SBM - Discharge to Federal waters (Gulf of Mexico, Cook Inlet, AK)	Base fluid retained on cuttings	≤ 6.9% olefin (weighted average) or ≤ 9.4% ester (weighted average)
	Sediment toxicity	Stock base fluid and discharged cuttings can be no more toxic to marine amphipods than a C ₁₆ -C ₁₈ IO base fluid and IO-contaminated cuttings
	Formation oil	No discharge
	Diesel fuel oil	No discharge
	Mercury	≤ 1 mg/kg dw in stock barite
	Cadmium	≤ 3 mg/kg dw in stock barite

Table 9. Continued

Waste Source and Receptor Body	Pollutant Parameter	Effluent Limitation
	Polycyclic aromatic hydrocarbons	≤ 10 mg/kg based on phenanthrene/wt of stock base fluid
	Biodegradation rate	Biodegradation rate in 120-day anaerobic test shall be no slower than that of a C ₁₆ -C ₁₈ IO base fluid
Drill cuttings associated with SBM - Discharge to Federal waters of S. California	All	No discharge

^a State waters are defined as the territorial sea between the shore and 3 miles offshore; ^b LC50 is the median lethal concentration; ^c Federal waters are offshore waters > 3 miles from shore.

General and special permits may contain additional requirements for drilling mud and cuttings discharges. All permits contain specific requirements for:

- Monitoring frequency for compliance with different effluent guidelines;
- Analytical methods for chemicals in drilling fluids and cuttings and toxicity test methods;
- Reporting and record keeping. Results of monitoring activities usually are submitted periodically to EPA in a Discharge Monitoring Report (DMR).
- Technical and operational requirements.

In writing a new permit, each EPA region may add special requirements specific to the outer continental shelf region under their jurisdiction. For example, permits for the Gulf of Mexico include the following requirements:

- No discharge of drilling wastes within 1000 m of (Region 4) or into (Region 6) an Area of Biological Concern;
- Used oils from the platform may not be added to drilling muds to be discharged from the platform;
- The rate of WBM and cuttings discharge from a single platform may not exceed 1000 bbl/hr (159,000 L/hr);
- The operator must maintain and report an inventory of all chemical additives to drilling muds destined for ocean disposal.

Special requirements for California (Region 9) include:

- Maximum permissible volume of drilling mud and cuttings discharge is set for each offshore platform and ranges from 50,000 bbl/year (7.95 million L/y) to 240,000 bbl/year (38.2 million L/y).
- Used oils from the platform may not be added to drilling muds to be discharged from the platform.
- The operator must maintain and report an inventory of all chemical additives to drilling muds destined for ocean disposal.
- Toxicity test limit for drilling fluids can be met by using one of eight generic drilling muds with approved additives. Toxicity of additives may have to be determined.
- Discharge of SBM and cuttings is not permitted.

Permits for Cook Inlet, Alaska and the Beaufort Sea (Region 10) include the following requirements:

- Rate of drilling fluid and cuttings discharge is set on a case-by case basis, based on water depth and ranges from 0 to 1000 bbl/hr (159,000 L/hr).
- Drilling wastes from no more than five wells can be discharged at one location.
- The operator must prepare and submit a mud plan outlining the types of drilling muds and additives to be used.
- The operator must maintain an inventory of all the drilling mud additives actually used.
- Restrictions are placed on setbacks from sensitive environments and in ice-covered areas.
- The operator must perform an environmental monitoring program to evaluate the impacts of drilling discharges on the marine environment.
- Additional monitoring is required for concentrations of barium, cadmium, chromium, copper, mercury, and lead in drilling fluids.

3.2 WBM and Cuttings Discharge Practices

Offshore discharge is limited to those drilling muds and cuttings that meet the local regulatory requirements. As discussed above, only WBM and cuttings generated with WBM or SBM are permitted for disposal to Federal waters of the US, if they meet ELG requirements. Usually, the cuttings recovered from the solids control equipment on the platform are flushed with seawater into a central discharge pipe (shunt line) that releases the cuttings just above or below the sea surface (CAPP, 2001). Occasionally, if the platform is in an environmentally sensitive area, EPA may require that the shunt line extend to near the sea floor (e.g., near the Flower Gardens Banks in the western Gulf of Mexico). Cuttings are discharged continuously during actual drilling, which usually occurs about half the time during drilling of a well. Drill cuttings containing 5 to 10 percent adsorbed WBM solids usually are discharged to the ocean at a rate of 0.2 to 2 m³/hour (53 to 530 gallons/hour) (Neff et al., 1987).

If permitted by the NPDES permit, WBM in volumes of about 20 to 30 m³ (5300 to 8000 gallons) per discharge are discharged to the ocean intermittently, usually from the mud settling pits, at rates of 80 to 300 m³/hour (21,000 to 79,250 gal/hour) during drilling. Small discharges usually occur every 1 to 2 days and last less than 5 to 20 minutes (Neff et al., 1987; Steinhauer et al., 1992). There may be a bulk discharge of as much as 200 m³ (53,000 gallons) of used WBM at the end of drilling, particularly following drilling of an exploratory well. This bulk discharge may last less than 1 hour, unless this would exceed the discharge rate limitation in the ELG (usually ≤ 1000 bbl/hr: 42,000 gal/hr).

Between the end of 1986 and early 1989, a total of 39 wells were drilled with WBM from three platforms in the Point Arguello Field off southern California. Approximately 256,000 bbl of WBM and 34,000 bbl of drill cuttings were discharged (Steinhauer et al., 1992). Cuttings were discharged continuously during active drilling. Drilling mud discharges were intermittent, varying from 0 to more than 3,100 bbl/day. Most discharges were of more than 310 bbl. There were several large discharges of drilling mud during drilling of each well. These bulk discharges occur when the mud engineer needs to substantially change the composition of the drilling mud or when the volume of drilling mud increases to the capacity of the mud pit on the platform.

The total mass of drilling mud and cuttings solids discharged to the ocean during drilling of a well varies widely, depending on the depth of the well, the drilling mud management strategy used, and the formation pressures encountered. A total of 900 metric tons of WBM and 1100 tons of cuttings may be discharged during drilling of an exploration well (Neff et al., 1987). Smaller masses of mud and cuttings would usually be discharged during drilling of a development well. A total of 420 million lbs (190,500 metric tons) of drilling mud solids were discharged to the Gulf of Mexico in 1998 during drilling of 559 wells

and a nearly equal amount was discharged during drilling of 43 deep-water wells (Table 3). This represents 340 metric tons/well in shallow water and 4420 metric tons/well in deep water.

3.3 Drilling Mud and Cuttings Dispersion

Although the total volumes of WBM and cuttings discharged to the ocean during drilling a well are large, the impacts in the water column environment are minimal, because discharges of small amounts of materials are intermittent and take place only during drilling operations spaced over a few to several months. Drilling mud solids do not increase to high concentrations in the water column and affect only small parcels of water. Periodic, minor increases in the turbidity and suspended particulate material concentrations in the upper water column during mud and cuttings discharges are unlikely to have an environmentally significant effect on phytoplankton, zooplankton, and pelagic animal communities in the vicinity of the drill rig (National Research Council, 1983).

WBM and cuttings are composed of a slurry of particles with a wide range of grain sizes and densities in water. Clay, silt, and most cuttings solids have densities of about 2.3 to 2.65 g/cm³; drilling mud barite has a density of about 4.3 g/cm³ (Nedwed, 2004). Silts and clays, as well as drilling mud barite, have diameters of less than about 74 μm (Figure 3). Particle diameter has a greater influence than density on the rate of settling of WBM and cuttings particles. Unflocculated clay and silt-sized particles, including barite, settle in calm water at a rate of about 3.7x10⁻² to 9.0x10⁻⁵ ft/s (Brandsma and Smith, 1999). However, bentonite clay in a WBM usually flocculates upon dilution in seawater (Muschenheim and Milligan, 1996; Curran et al., 2002). The clay floc is a loose aggregate of clay particles that may include barite particles. These aggregates settle more rapidly than unflocculated silt and clay. Cuttings particles, which span a size range from clay to gravel (Figure 3), settle in seawater at a rate of about 8.5x10⁻¹ to 4.4x10⁻⁶ ft/sec (Nedwed, 2004).

When WBM and cuttings are discharged to the ocean, the larger particles, representing about 90 % of the mass of the mud solids, form a plume that settles quickly to the bottom (or until the plume entrains enough seawater to reach neutral buoyancy). About 10 % of the mass of the mud solids consisting of fine-grained unflocculated clay-sized particles and a portion of the soluble components of the mud form another plume in the upper water column that drifts with prevailing currents away from the platform and is diluted rapidly in the receiving waters (Ayers, et al., 1980; Brandsma et al., 1980; National Research Council, 1983) (Figure 4). The fine-grained solids in the upper plume settle slowly over a large area of the sea floor.

Several field studies have shown that drilling muds discharged to the ocean are diluted rapidly to very low concentrations, usually within 1000 to 2000 m down-current from the discharge and in less than an hour after the discharge. In areas where water current speeds are high, dilution of drilling mud and cuttings discharges is very rapid; discharges from an exploratory drilling rig in Cook Inlet were diluted by 10,000-fold within 100 m of the rig (Houghton et al., 1980b). In well-mixed ocean waters, drilling mud is diluted by more than 100-fold within 10 m of the discharge. A 43 m³ discharge of drilling mud from a platform off the coast of southern California, USA, was diluted by 183-fold at 10 m and by 1,049-fold at 100 m (O'Reilly et al., 1989).

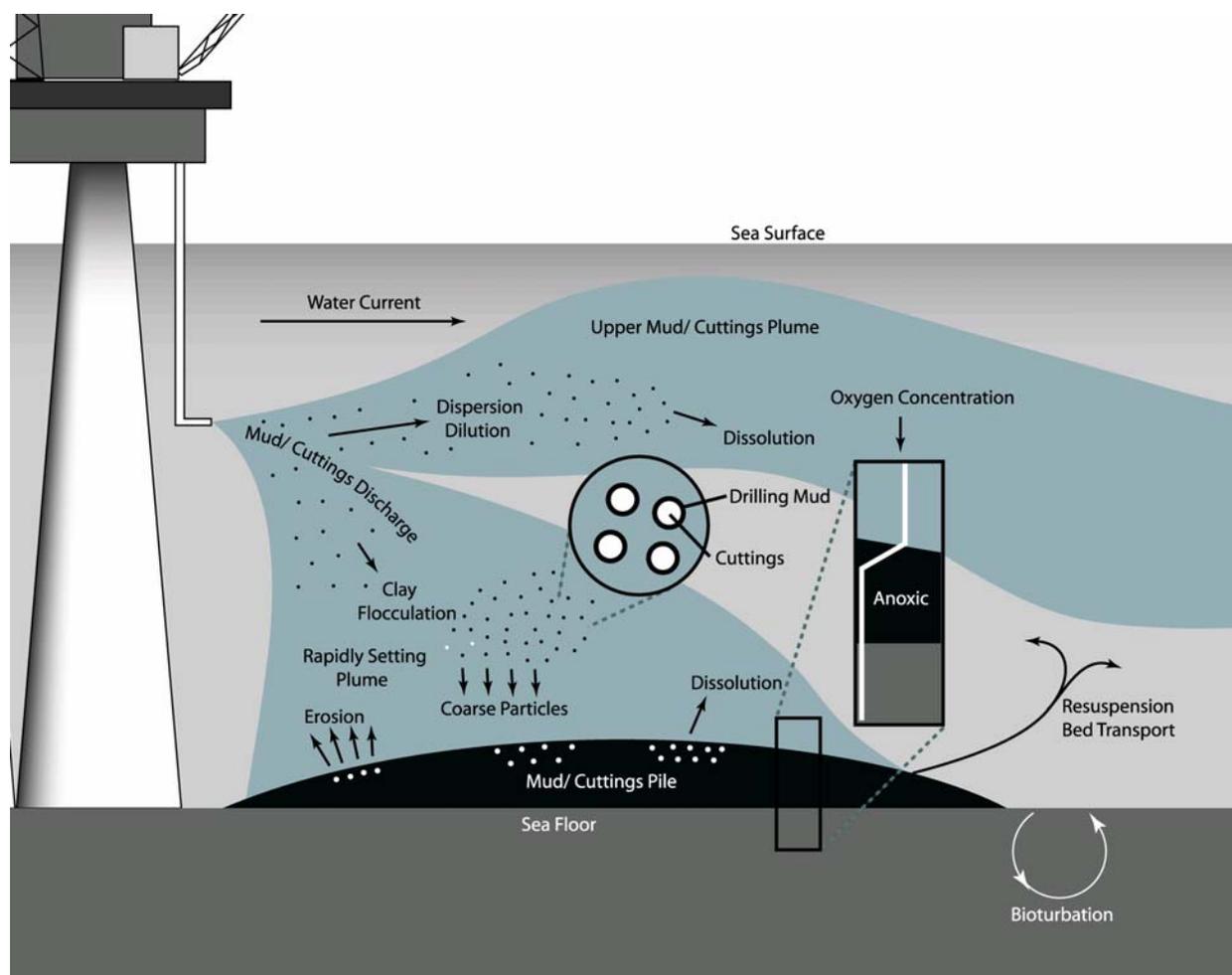


Figure 4. Dispersion and fates of water based drilling mud (WBM) following discharge to the ocean. The WBM forms 2 plumes, an upper plume, usually representing ~ 10 % of the mass of discharged solids, containing fine-grained unflocculated solids and dissolved components of the mud, and a lower, rapidly-settling plume containing dense larger-grained particles, including cuttings, and flocculated clay/barite particles. The WBM solids undergo dispersion, dilution, dissolution, flocculation, and settling in the water column. If the WBM contains a high concentration of organic matter, the cuttings pile may become anaerobic near the surface. The cuttings pile is altered by redox cycling, bioturbation, and bed transport.

Recent WBM dispersion modeling confirms the rapid dilution of WBM and WBM cuttings in the receiving water environment (Nedwed et al., 2004; Smith et al., 2004). Ayers (1994) used the Offshore Operators Committee (OOC) mud and cuttings model to predict the dilution and fate of a 1-hour WBM discharge at a rate of 160 m³/hr to offshore waters of Sakhalin Island in the Russian Far East. The predicted drilling mud plume extended for several hundred meters down-current at the end of the discharge (Figure 5). The suspended solids concentration in the plume dropped from 300,000 mg/L (ppm) at the source to less than 8 ppm at 750 m after a transport time of 1 hour. A 1000-fold dilution was predicted at a transport time of about 10 minutes at a distance of about 100 m from the platform. The US aquatic toxicity ELG for WBM is 30,000 ppm suspended particulate phase (equivalent to 3,000 ppm drilling mud). The concentration of WBM in the plume drops below this safe concentration within about

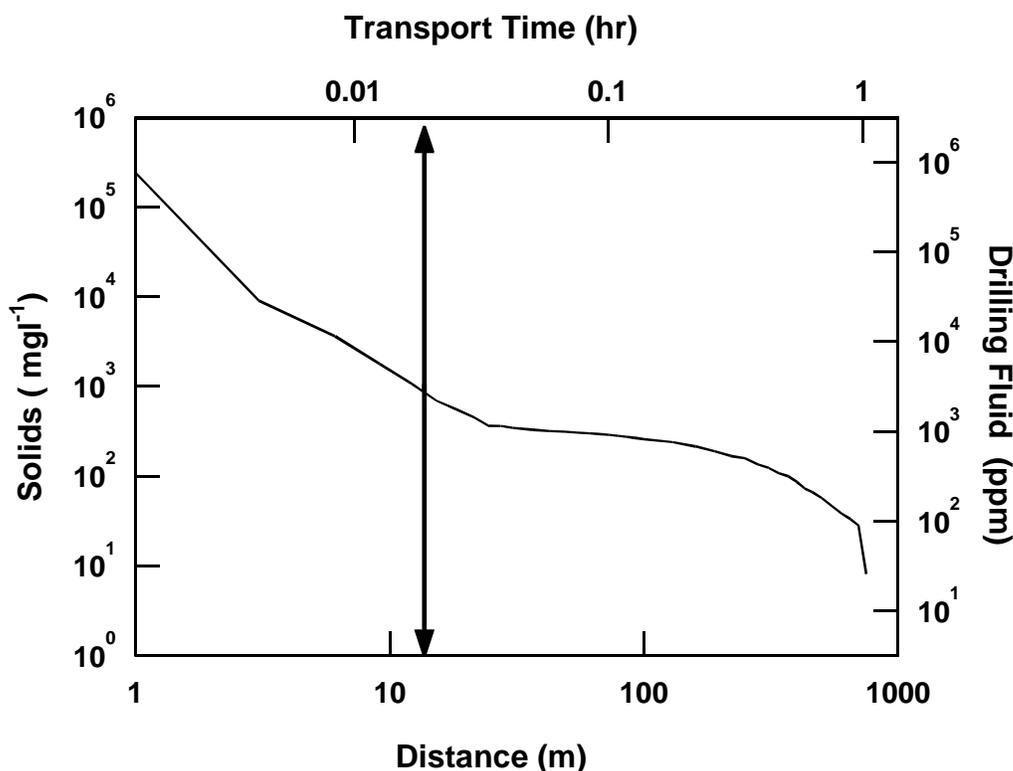


Figure 5. Predicted concentrations of drilling mud solids in the water column with distance and transport time (the time required for a parcel of fluid moving with the current to reach a particular distance) during a 160 m³/hr WBM discharge lasting 1 hour offshore Sakhalin Island, Russia. The solids concentration dropped from 300,000 ppm at the source to less than 8 ppm at 750 m and a transport time of 1 hour. The vertical arrows show the drilling distance at which the solids reached 3,000 ppm, corresponding to the toxicity limit for drilling muds in the ELG for drilling discharges issued by the U.S. EPA. The solids fell below this concentration within 15 m of the discharge. From Ayers (1994).

2 minutes of the discharge about 15 m downcurrent. Thus, marine organisms that may become entrained in or swim through the WBM discharge plume are unlikely to be adversely affected by it.

3.4 Accumulation of WBM and Cuttings Solids in Sediments

WBM solids and drill cuttings settle to and accumulate on the bottom. The distance from the platform and the amount of discharged solids accumulating depend primarily on current speeds and water depths. In low-energy, shallow water environments, much of the mud and cuttings may settle on the bottom within 10 to 20 m of the platform (National Research Council, 1983). These deposits usually are not toxic if WBM and WBM cuttings are discharged; however, changes in the biological community may occur as a result of physical alterations of the benthic habitat.

At a few locations in the Gulf of Mexico, drilling mud and cuttings were shunted in a pipe to near the bottom and discharged within about 10 m of the seabed. This was the practice during development of the gas resources at some facilities in the High Island Lease Area, near the Flower Gardens Banks off Texas/Louisiana (Kennicutt, 1995). Shunting was used to protect the coral reefs at the top of the bank from suspended solids associated with the discharged mud and cuttings. When shunting is practiced, the

mud and cuttings solids accumulate in a large pile directly under and in a small area near the end of the shunt pipe. Shunting prevents wide dispersal of the discharged solids, so elevated concentrations of mud and cuttings ingredients are localized near the point of discharge. This practice was effective near the Flower Garden Banks in preventing mud and cuttings solids from spreading to and depositing on the sensitive coral reef community at the top of the bank. However, it did result in a localized accumulation of a large amount of solids and associated chemical contaminants on the bottom in a small area near the end of the discharge shunt pipe.

Large-grained cuttings particles may settle rapidly and accumulate in large amounts on the sea floor near the platform. There are clear gradients of sand concentration in sediments near three platforms in the Gulf of Mexico monitored as part of the GOOMEX Program (Table 10). The platforms are in 30 to 157 m of water and 6 to 18 wells had been drilled from each. EPA required shunting of drilling mud and cuttings to within 10 m of the bottom at 2 of the platforms. Mean sand concentration in sediments near the platforms decreased from about 60 percent at 50 m to 12.6 percent at greater than 3000 m (background) from the platform. The excess sand probably was derived primarily from drill cuttings discharges, but could also have come in part from discharges of produced sand. Produced sand is no longer permitted for discharge to US offshore waters. There also was a decreasing gradient of sediment total organic carbon (TOC) concentration with distance from the platforms, which also could have come from either drill cuttings or produced sand deposition.

Table 10. Relationship between distance from three production platforms in the western Gulf of Mexico and mean concentrations of sand and total organic carbon (TOC) in surficial sediments. From Kennicutt et al. (1996a).

Distance from Platform (m)	Percent Sand	Percent (TOC)
50	60.5	1.02
100	49.2	0.98
200	21.9	0.89
500	13.8	0.69
≥3000	12.6	0.61

If discharges are at or even above the sea surface, which is a common practice, the mud and cuttings plume is diluted and dispersed over a wide area and the solids are distributed as a thin veneer over a large area of the sea floor. In such cases, concentrations of drilling mud and cuttings chemicals in sediments usually are only slightly elevated above natural background levels. Current guidelines recommend discharge below the sea surface. Hyland et al. (1994) modeled fluxes of drilling mud solids to the sea floor near Platform Hidalgo off California, based on drilling mud and cuttings discharge data collected during drilling. During peak drilling activity, maximum fluxes were predicted to the sea floor within about 1.5 km of the platform of 400 to 500 mg/m²/day, representing about 2 percent of the flux of suspended natural particles to sediments in this area.

Smith (2003) modeled the dispersion and deposition of WBM and WBM cuttings in deep water (Figure 6). The solids settled and accumulated over a wide area of the sea floor, mostly along the axis of the net tidal current ellipse. The predicted maximum loading of drilling waste solids on the sea floor was 64 kg/m² in a small area adjacent to the platform. Loadings to about 0.1 kg/m² in sediments extended to about 1000 m from the platform. Predicted increments in sediment barium concentration (from drilling mud barite) ranged from nearly 20,000 ppm near the platform to about 30 ppm where sediment loading with waste solids was 0.1 kg/m². The drilling waste accumulated on the bottom to a maximum estimated depth of about 4 cm.

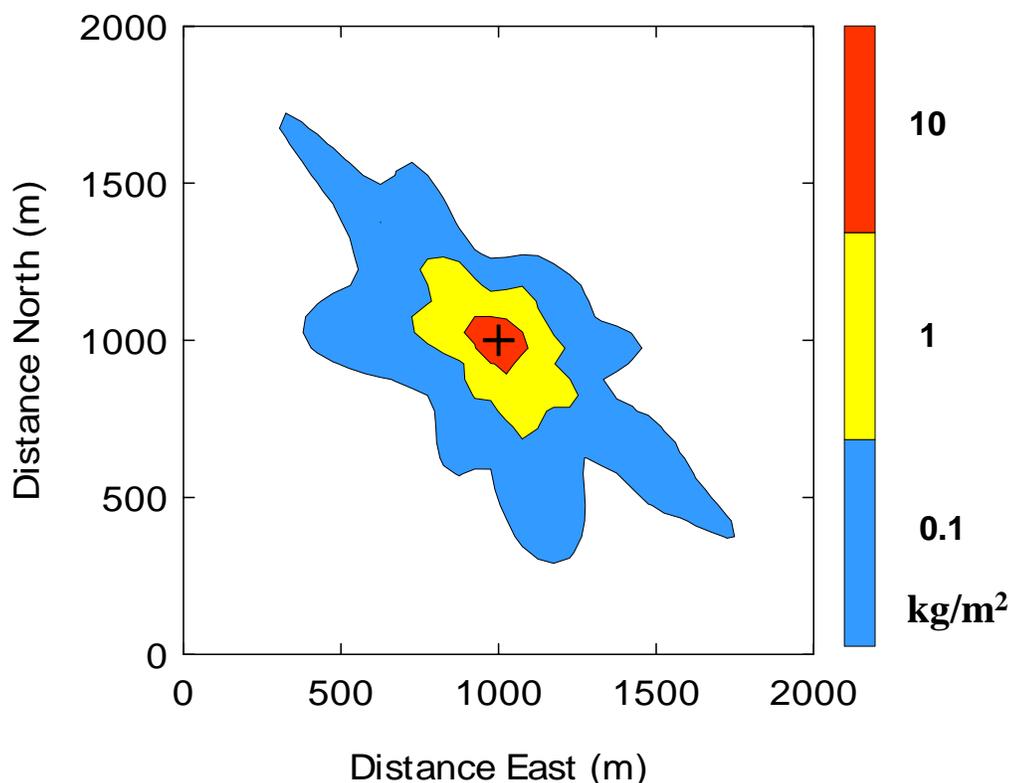


Figure 6. Modeled distribution and loading of WBM/cuttings solids on the sea floor following drilling mud and cuttings discharges to offshore waters. Maximum loading of the sea floor with drilling solids was about 64 kg/m^2 , representing a thickness of solids of about 4 cm. The increment in barium concentration in the cuttings pile is approximately 308 ppm Ba/kg/m² of solids loading. From Smith (2003).

By comparison, many cuttings piles in the North Sea are more than 1 meter deep (Hartley et al., 2003). This is because OBM cuttings (which do not disperse as effectively as WBM cuttings in the water column) often were shunted to just above the sea floor at many large North Sea developments (Bell et al., 2000). WBM and WBM cuttings disperse in the water column over a wide area and settle as a thin veneer over a large area of the sea floor, particularly in deep water or high-energy marine environments. However, OBM and SBM cuttings, being “oil-wet”, tend to clump and settle rapidly as large particles over a small area near the platform, often producing a deep cuttings pile directly below the discharge pipe (Neff et al., 2000).

3.5 Accumulation of Chemicals from WBM and Cuttings in Sediments Near Offshore Platforms

3.5.1 Petroleum Hydrocarbons.

It was common practice in the past, but is less common today, to add diesel fuel or mineral oil to WBM to aid in lubricating the drill string or to aid in freeing stuck pipe. The refined oil in WBM and cuttings can be identified in environmental samples by its hydrocarbon signature. Diesel fuels and mineral oils have characteristic saturated and aromatic hydrocarbon assemblages that that can be identified in environmental samples by suitable fingerprinting methods (Boehm et al., 1989).

Sediments near platforms where only WBM and WBM cuttings were discharged usually do not contain high concentrations of total petroleum hydrocarbons (TPH) and PAH. Surficial sediments near 3 platforms in the Gulf of Mexico with a long history of drilling and production contained up to 400 mg/kg TPH and 1 mg/kg total PAH (Table 11). There was a good correlation between barium and hydrocarbon concentrations in the sediments, indicating that most of the hydrocarbons probably came from drilling mud and cuttings discharges. Produced water from the Gulf of Mexico usually contains a high concentration of barium which precipitates as barite when the produced water is discharged to the ocean (Neff, 2002a). Thus, produced water could be an additional source of the barium and hydrocarbons in sediments near the platforms, particularly in shallow water (Neff et al., 1992).

Table 11. Chemical Characteristics of surface sediments near 3 platforms with a long history of drilling and production discharges to the U.S. Gulf of Mexico. From Kennicutt (1995).

Parameter ^a	Platform Lease Block		
	MAI-A686	MU-A85	HI-A389
Eh (mV)	-93 to +204	-93 to +268	-92 to +233
TOC (%)	0.1 – 1.5	0.2 – 1.5	0.4 – 2.5
Barium (mg/kg)	653 – 4,680	720 – 26,250	785 – 280,200
TPH (mg/kg)	0 – 119	0 – 382	0 406
TPAH (mg/kg)	0.008 – 0.59	0.013 – 6.36	0.011 – 1.24

^a Eh redox potential; TOC total organic carbon concentration; TIC total inorganic carbon concentration; TPH total petroleum hydrocarbons determined by GC/FID; TPAH total polycyclic aromatic hydrocarbons (>40 analytes) determined by GC/MS.

Drill cuttings containing low concentrations of TPH and PAH were discharged to the outer continental shelf at the Point Arguello Field off California during drilling of 39 wells from three platforms (Table 8). Although there was a slight increase in total hydrocarbons in sediments near Platform Hidalgo during drilling (from a mean of 42 $\mu\text{g/g}$ to 103 $\mu\text{g/g}$), there was not a significant increase in the mean concentration of total PAH in the sediments (Steinhauer et al., 1994). Total PAH concentration in sediments over 4 years before to 1 year after drilling ranged from 0.01 to 0.2 $\mu\text{g/g}$, and most probably was derived from biogenic (e.g., perylene), pyrogenic (combustion), or oil seep sources.

Similar observations were made during drilling of several exploratory wells on Georges Bank off New England (Neff et al., 1989a; Phillips et al., 1987). Although small amounts of diesel fuel were used in drilling muds for 1 rig, there was only a slight increase in TPH and PAH concentrations in a few sediment samples near the discharge site after drilling. Total PAH concentrations in sediments near the rig never exceeded the range of background PAH concentrations for outer continental shelf sediments from the region (Boehm and Farrington, 1984), and returned rapidly to pre-drilling concentrations shortly after completion of drilling.

3.5.2 Metals.

The metals composition of WBM and cuttings resembles that of natural marine sediments (Tables 4 and 7). However, concentrations of several metals usually are significantly higher in drilling muds and mud/cuttings discharges than background concentrations in uncontaminated marine sediments (Tables 4 and 12). Barium (from drilling mud barite) often is the most abundant metal in WBM and cuttings. The other metals sometimes present at substantially higher concentrations in drilling muds than in natural marine sediments are chromium, lead, and zinc. Because of its abundance in drilling muds, barium is used most frequently as an indicator of drilling muds in sediments. Concentrations of dense, insoluble barite often are extremely high in most WBM, OBM, and SBM (spud muds used to drill the near-surface hole

often contain little or no barite). Barium concentrations greater than about 2,000 mg/kg in soils and sediments suspected of being contaminated with drilling wastes may indicate the presence of drilling muds or cuttings. However, it is important to recognize that some clean natural soils and sediments may contain up to 8,000 mg/kg barium (Neff, 2002a). It is important, in using barium as an indicator of drilling mud and cuttings in sediments, that the appropriate extraction and analytical methods be used to analyze barium in the environmental samples. Most extraction methods do not remove all the barium from sediments (Hartley, 1996). Barium actually is a tracer of only the most abundant solid ingredient in drilling mud: barite. Other drilling mud ingredients may have different dispersion and deposition patterns than barite and, therefore may have a different distribution and persistence in sediments near drilling mud and cuttings discharges (Continental Shelf Associates, 2004).

Concentrations of other metals, most of them associated with barite, also may be elevated above background concentrations in sediments containing drilling muds and cuttings. However, true background concentrations of most metals in sediments are geographically variable and often are not well understood for most locations. The increment in metals concentrations due to drilling muds and cuttings may be difficult to estimate. Frequently, concentrations of one or a few metals, particularly chromium, lead, and zinc, are elevated above expected background concentrations in sediments near the drilling site (Table 12), and probably were derived from the drilling discharges (Boothe and Presley, 1985, 1989; Neff et al., 1989a; Steinhauer et al., 1994; Sheahan et al., 2001; Pozebon et al., 2005).

Table 12. Concentrations of several metals in nearfield sediments before and after drilling several wells on Platform Hidalgo in the Point Arguello Field off California. Mean metals concentrations in WBM and cuttings discharged from the platform are included. Concentrations are $\mu\text{g/g}$ dry wt (ppm). From Steinhauer et al. (1992, 1994).

Metal	Mean WBM	Mean Cuttings	Sediments (after drilling)	Sediments (before drilling)
Barium	108,000	5200	940	703
Silver	0.3	0.6	0.09	0.14
Arsenic	6.3	10	8.5	6.5
Cadmium	1.2	2.3	0.54	0.72
Copper	30	48	16	21
Chromium	85	150	121	99
Mercury	0.13	0.10	0.07	0.07
Nickel	41	67	43	48
Lead	19	1900	14	14
Vanadium	71	110	56	81
Zinc	290	1300	71	71

Boothe and Presley (1985, 1989) evaluated the mass balance of several metals in sediments within 500 m of 6 exploration and production platforms in the western Gulf of Mexico. A small fraction (<1.5% inshore and <12% offshore) of the barite used and discharged from the platforms was identified as excess barium in sediments within 500 m of the platforms. The remainder probably was swept away by storm-induced bed transport. There were significant increases above background in concentrations of zinc (5- to 10-fold) and mercury (4- to 7-fold) in sediments at 2 offshore platform sites. The amounts of excess zinc and mercury in the sediments were inversely correlated with distance from the platform and directly correlated with the excess barium in sediments, indicating that the excess metals probably were associated with drilling waste solids. Although there was a relationship between concentrations of the other metals

examined (Cd, Cr, Cu, Pb) and barium in sediments, concentrations of these metals were not elevated significantly above background in sediments near the drilling sites.

About 65,000 bbl of WBM and cuttings were discharged to the ocean during drilling of 7 wells from Platform Hidalgo in the Point Arguello Field off California (Steinhauer et al., 1992). The WBM and cuttings discharged from the platform contained several metals at concentrations comparable to typical concentrations in muds and cuttings from the Gulf of Mexico and North Sea (Table 7 and 12). Concentrations of most metals in sediments near the platform were similar before and after the drilling discharges. Concentrations of only barium and possibly chromium were elevated during and for a short time after drilling.

Neff et al. (1989a) reported similar results for sediments near exploratory drilling rigs on Georges Bank off the New England coast. Barium and chromium were the only metals identified at higher than background concentrations in sediments near the platform. Slightly elevated concentrations of barium were detected in the silt-clay fraction of sediments up to 65 km downcurrent from one of the drilling rigs. The estimated half-life of excess barium in the sandy sediments near the exploratory rigs was 0.4 years. Loss of fine-grained barite from sediments probably was primarily caused by storm-induced bed transport.

Elevated concentrations of barium were detected in fine grained sediments in depositional areas of the Skagerrak, an arm of the North Sea between Norway and Denmark (Lepland et al., 2000). The barium apparently was derived from drilling mud barite discharged to offshore waters of the southern North Sea, lending support to the hypothesis that drilling mud and cuttings solids can be dispersed over large areas by ocean currents. The nearest oil production field, the Ekofisk Field is more than 100 km west of the Skagerrak.

Similar results were obtained in a recent monitoring study in the Gulf of Mexico (Table 13). Both WBM and SBM were used on both platforms and drill cuttings were discharged over several years. There was little difference in concentrations of any metals, except barium, in near-field and far-field sediments (Continental Shelf Associates, 2004). Barium concentrations were orders of magnitude higher in some near-field sediment samples than in the single far-field samples collected from each location.

Concentrations of cadmium, copper, mercury, and lead in some near-field sediments (<100 m from the discharge) were higher than in far-field sediments (>3,000 m), particularly at the discharge site at Mississippi Canyon 496 in 556 m of water (Table 13). Mercury was enriched in near-field sediments relative to far-field sediments at MC 496, but not in near-field sediments at MP 299. Mercury also was enriched in near-field sediments at four of the other discharge sites monitored in this study (Trefry et al., 2002). Highest mercury concentration was in a near-field (<100 m) sediment sample from Ewing Bank 963 in 540 m of water. The excess mercury in near-field sediments probably was associated with drilling mud barite. The average concentration of mercury in the barite used at the eight discharge sites monitored in the Screening and two definitive cruises performed by Continental Shelf Associates (2004) was estimated to be 0.59 mg/kg, based on Hg/Ba concentration ratios in near-field sediments.

Table 13. Concentrations of several metals in surficial sediments from near-field (<100 m) and far-field (>3000 m) zones of two drilling mud and cuttings discharge sites in the Gulf of Mexico. Both platforms discharged both WBM and SBM cuttings. Concentrations are $\mu\text{g/g}$ dry wt (ppm). From Trefry et al. (2002) and Continental Shelf Associates (2004).

Metal	Main Pass 299		Mississippi Canyon 496	
Water Depth (m)	83		556	
Wells Drilled	450		5	
Total Cuttings Discharge (bbl)	27,692		4654	
Sample Location	Near-Field ^a	Far-Field ^b	Near-Field ^a	Far-Field ^b
Arsenic	5.3 – 10	8.3	11 – 21	14
Barium	4200 – 34,800	848 – 3640	2110 – 358,000	750 - 1060
Cadmium	0.12 – 0.24	0.15	0.13 – 0.72	0.23
Chromium	59 – 87	93	17 – 70	77
Copper	19 – 25	20	20 – 89	27
Mercury	0.05 – 0.07	0.05 – 0.07	0.07 – 0.15	0.06 – 0.09
Nickel	14 – 33	29	6.0 – 30	31
Lead	18 – 52	26	27 – 77	30
Vanadium	98 – 164	136	10 – 136	139
Zinc	96 – 159	120	34 – 147	128

^a Range for all samples.

^b Only one far-field sediment sample was analyzed for all metals, except barium and mercury, which were analyzed in six replicate far-field samples.

3.5.3 Solubility of Barite.

Most of the metals in drilling muds and cuttings on the sea floor are associated with drilling mud barite. These metals are relatively immobile and non-bioavailable to bottom-living animals because of the low solubility of barite in seawater and even in anoxic marine sediments. The solubility of barite in marine sediments and drill cuttings piles is controlled by sulfate concentration in sediment pore water (Monnin et al., 2001). As sediment oxygen is depleted by microbial degradation of organic matter, sulfate reducing bacteria use sulfate as an alternate electron source and generate sulfide that combines with and precipitates sediment metals (Hartley et al., 2003). If barite concentration in sediments is high, it can serve as a source of reducible sulfate for sulfate reducing bacteria (Ulrich et al., 2003), releasing dissolved barium into the pore water (Phillips et al., 2001). Much of the barium released into sediment pore water by the activity of sulfate reducing bacteria diffuses upward to the oxic layers of the sediment or into the overlying water column, where it precipitates with sulfate in the oxygenated water phase (Paytan et al., 2002). Thus, barite is highly persistent in marine sediments and drill cuttings piles.

Trefry et al. (1986) and Trefry (1998) have shown that even under hypoxic or anoxic conditions that occur frequently in sediments near offshore platforms, very little barite dissolves. Shimmield et al. (2000) reported a maximum concentration of 450 $\mu\text{g Ba/kg}$ sediment of dissolved barium (in sediment pore water) just below the surface of the Beryl A cuttings pile in the North Sea. This concentration exceeds the seawater solubility of barium, estimated at 37 to 52 $\mu\text{g/L}$, depending on temperature, salinity, and sulfate concentration (Chow and Goldberg, 1960; Church, 1979). Much of the barium in cuttings pile pore water probably was present as complexes with pore water dissolved or colloidal organic matter or as precipitated microscopic crystalline and amorphous barite particles (Hartley et al., 2003). Bulk sediment at this depth in the pile contained more than 50,000 mg/kg total particulate barium. Thus, barite may

dissolve slowly into pore water of anoxic, sulfidic sediments, the rate controlled by the low solubility of barium in marine waters.

Little dissolved, uncomplexed barium escapes from the sediment into the overlying water column; most precipitates as barite because continental shelf bottom seawater is nearly saturated with respect to barium sulfate. The concentration of dissolved barium in the marine water column is in equilibrium with barite; maximum saturation is just above the sea floor at water depths of about 1000 m in the Atlantic Ocean (Monnin et al., 1999; Rushdi et al., 2000). In any case, dissolved barium, at the concentrations at which it can occur in seawater or sediment pore water, is not toxic to marine organisms (Neff and Sauer, 1995; Neff, 2002a).

Most of the metals in drilling mud barite are present as insoluble metal sulfide inclusions in the barite particles. The long-term fate of metals introduced to sediments as solid sulfides, as occurs when drilling muds and cuttings are deposited on the sea floor, depends on the stability in the sediments of sulfides (Trefry, 1998). The stability of sulfides in sediments depends on the oxidation/reduction (redox) potential (Eh) and pH of the sediment. Typical redox potentials (Eh) in marine sediments range from +100 mV to -400 mV; pH usually is in the range of 7 to 8 (neutral or slightly alkaline). Sulfide minerals are stable under reducing conditions (Eh below about 0 mV) and neutral or alkaline pH. The Eh of continental shelf and slope sediments, where most production platforms occur, usually decreases to below 0 mV at a depth of about 5 to 50 cm below the sediment surface (Presley and Trefry, 1980). The redox potential discontinuity (RPD: where Eh falls to 0 mV) usually is less than 1 cm below the surface in mud and cuttings piles on the outer continental shelf of the North Sea (Shimmield et al., 2000) and in outer continental shelf and slope sediments in the Gulf of Mexico where synthetic SBM cuttings have accumulated (Continental Shelf Associates, 2004). This probably also is the case in sediments near offshore platforms in the Gulf of Mexico where fouling organisms falling off submerged platform structures cause organic enrichment in the sediments, leading to oxygen depletion. Schaanning et al. (1996) showed that mercury and most other metals, except possibly lead, associated with anoxic sediments of cuttings piles do not dissolve from the barite and leach into sediment pore water and are not bioavailable to benthic marine animals. Dissolution of barite under reducing conditions when sulfate concentrations are low does not result in dissolution of metal sulfide inclusions in the barite (Trefry et al., 1986; Trefry, 1998).

Barite is extremely stable and insoluble in sea water under oxidizing conditions (high oxygen concentration and redox potential) at the surface of the mud/cuttings accumulation. Some metal sulfides may be slightly soluble under oxidizing conditions (Morse, 1994). However, those associated with barite particles are protected from dissolution by the surrounding barite matrix.

3.5.4 Fate of Mercury in Barite.

The greatest concern about possible environmental impacts of metals associated with drilling waste discharges to the Gulf of Mexico is about mercury (Neff, 2002b). Even under oxidizing conditions (Eh > 0 mV), mercuric sulfide is extremely stable and does not dissolve rapidly, particularly if the concentration of sulfate is high, as is the case in marine sediments (Trefry, 1998). Thus, mercury in metal sulfide inclusions in barite from deposited drilling muds and cuttings is highly stable and insoluble in sediments near offshore platforms. It is not bioavailable to marine organisms. Nelson et al. (1984) showed that plants did not bioaccumulate mercury from agricultural soils amended with a high trace metal barite, confirming that mercury associated with sulfide inclusions in barite is not bioavailable even under oxidizing conditions.

The concentration of mercury in sediments near a large number of drilling waste discharge sites in the Gulf of Mexico range from less than 0.01 to 3.5 ppm dry wt (Neff, 2002b). The background concentration

for offshore sediments in the Gulf of Mexico usually is in the range of 0.01 to about 0.2 ppm. The average concentration of mercury in marine sediments, worldwide is 0.19 ppm (Salomons and Föstner, 1984). Pelagic clays, such as those on the continental slope of the Gulf of Mexico, contain about 0.1 ppm mercury. Where concentrations in sediments exceed about 0.15 ppm, highest concentrations usually are in sediments closest to the platform and concentrations decrease with distance from the platform. Frequently, there is a good correlation between mercury and barium concentrations in sediments near drilling mud discharge sites, indicating that much of the excess mercury is associated with drilling mud barite.

The highest mercury concentration measured in sediments near a Gulf of Mexico platform was 3.5 ppm; the sediments were collected as part of the GOOMEX program from the platform in lease area HI-A389 (Kennicutt, 1995). These sediments were collected near a platform from which used drilling mud and cuttings had been shunted to just above the bottom (Kennicutt et al., 1996b). Four sediment samples, two replicates each from two locations 24 and 33 m from the discharge from the platform at HI-A389, contained more than 2.9 ppm total mercury. Several other sediment samples collected within about 35 m of the outfall contained between 1.0 and 2.3 ppm mercury. These all are duplicate samples and represent sediments from 4 locations near the discharge. All other sediment samples collected during 4 field surveys to the platform (more than 200 samples in all) contained less than 0.5 ppm mercury. Thus, there was a very sharp gradient of decreasing sediment mercury concentrations with distance from this worst-case platform (Figure 7). Sediments collected more than about 100 m from the discharge contained essentially background concentrations of mercury. All of these wells were drilled before the <1 ppm limit on mercury in barite was imposed by EPA.

Concentrations of methylmercury were measured in sediments near 6 of the discharge sites monitored by Continental Shelf Associates (2004) in order to assess whether the insoluble, inorganic mercury associated with discharged drilling solids could be converted to toxic methylmercury in reduced layers of sediment near the discharge site (Trefry et al., 2002; Trefry, 2003). Although concentrations of total mercury were significantly higher in nearfield than in farfield sediments at 5 of the 6 discharge sites, concentrations of methylmercury were similar in nearfield and farfield sediments around all discharge sites. There was a strong correlation between barium and total mercury concentrations in the sediments, confirming drilling mud/cuttings barite as the likely source of the excess mercury in nearfield sediments. Methylmercury concentrations in nearfield sediments ranged from less than 0.00003 to 0.003 mg/kg, compared to concentrations of 0.0001 to 0.001 mg/kg in farfield sediments. When results for subsurface (2 to 20 cm) samples are included, there are no significant differences between methylmercury concentrations in nearfield and farfield sediments. Methylmercury represented less than 1 percent of total mercury in all sediments, which is typical for uncontaminated marine sediments (Neff, 2002b). Thus, it is probable that mercury from discharged drilling mud/cuttings in sediments near offshore drilling sites is not converted to methyl mercury and is not toxic to marine organisms living in or on the sediments.

Dissolved inorganic mercury can be converted to methylmercury by several groups of bacteria, mostly sulfide reducers, at and just below the RPD in sediments (Neff, 2002b). Methylmercury is bioavailable to marine animals and is persistent in tissues of marine organisms. It is the most toxic form of mercury to all plants and animals.

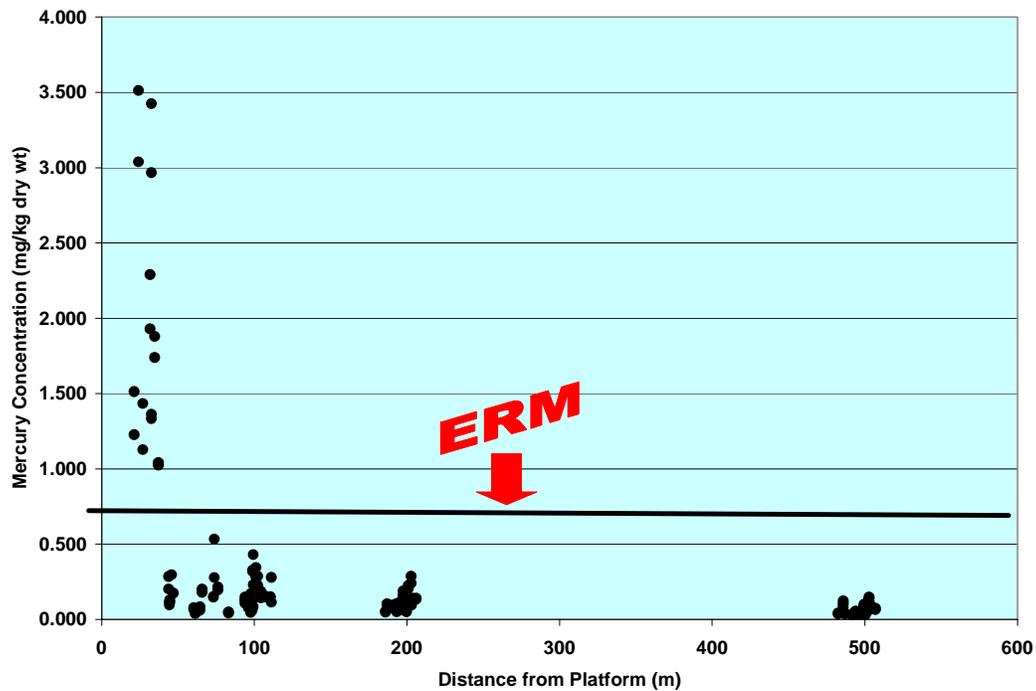


Figure 7. Concentrations of mercury in surface sediments collected at different distances from the drilling mud outfall pipe on Platform HI A389 near the Flower Garden Banks off the Texas/Louisiana coast. Drilling mud and cuttings were shunted to within 10 m of the bottom, resulting in accumulation of large amounts of solids on the bottom and a steep gradient of elevated barium and metals, including mercury, concentrations in bottom sediments. Highest concentrations were within 35 m of the outfall. The interim sediment quality guideline, Effects Range Median (ERM) value is shown for comparison. Data from Kennicutt (1995), as presented in Neff (2002b).

4.0 BIOLOGICAL EFFECTS OF WBM AND CUTTINGS IN THE OCEAN

4.1 Bioavailability of Drilling Mud and Cuttings Ingredients to Marine Organisms

4.1.1 *Forms Metals in WBM and Cuttings Accumulations in Marine Sediments.*

Bioavailability is the extent to which a chemical can be absorbed (bioaccumulated) by a living organism by active (biological) or passive (physical or chemical) processes (Neff, 2002a). A chemical is said to be bioavailable if it can move through or bind to a permeable surface coating (e.g., skin, gill epithelium, gut lining, cell membrane) of an organism (Newman and Jagoe, 1994). Metal bioavailability from sediments (cuttings piles) can be divided into 2 components: environmental accessibility and environmental bioavailability.

Environmental accessibility is a measure of the fraction of the total chemical that is in a form or location in the environment that is accessible for bioaccumulation by organisms. Metals of all forms in deep layers of sediment or cuttings have a low accessibility to marine organisms living in or on surface layers of the cuttings pile or in the overlying water column. The metals in cuttings piles are present primarily as insoluble inclusions in barite, clay, and cuttings particles. These solid metals are not bioaccessible. A small fraction of the total metal is in apparent solution in the pore water of the cuttings pile (Shimmield et al. 2000). If the cuttings pore water is accessible to marine organisms, or is mixed up into the overlying water column by sediment disturbance, some of the dissolved and colloidal metals in it may be in bioavailable forms and may be bioaccumulated by marine organisms.

Environmental bioavailability depends on the interactions of a marine organism with its environment. Exposure occurs at the interface between environmental media (water, sediment, and food) and permeable biological membranes of the marine organism in contact with the different media. Environmental bioavailability is controlled by the relative amount of permeable epithelia in contact with the different environmental media and the duration of contact, and the physical form of the chemical in the environmental medium. Dissolved, free ionic forms, some metal-organic colloid complexes, and low molecular weight organo-metal compounds (e.g., methylmercury, arsenobetaine) of metals are the most bioavailable forms of most metals to marine organisms (Neff, 2002a).

The most bioavailable fraction of metals in an accumulation of WBM and cuttings on the sea floor is that dissolved in the pore water or loosely complexed with particles. Deuel and Holliday (1998) fractionated the metals in a WBM and concluded that most of the total of all but one metal was in organic/sulphide complexes or the residual fraction, both considered inaccessible for bioaccumulation by marine organisms (Table 14). Nearly 50 percent of the lead and more than 20 percent of the cadmium, chromium, and zinc in the WBM sample were in the Fe-Mn oxide fraction, which dissolves under anoxic conditions in sediments, releasing adsorbed metals. Most of the metals not associated with the Fe/Mn oxides are present primarily in drilling mud barite in the WBM. They are associated with sulphide mineral inclusions (mainly sphaelerite: zinc sulphide) in the barite and are not soluble in anoxic marine sediment pore waters (usually high in dissolved sulphide) (Trefry et al., 1986; Neff, 2002a,b). The distribution of metals in different geochemical fractions of North Sea cuttings pile sediments is similar to that described by Deuel and Holliday (1998) for U.S. WBM (Westerlund et al., 2001, 2002). About 17 percent of the lead and 36 percent of the nickel in North Sea cuttings piles are in potentially bioavailable forms.

Table 14. Percent distribution of metals among geochemical fractions in a WBM. From Deuel and Holliday (1998).

Fraction	Arsenic	Barium	Cadmium	Chromium	Lead	Zinc
Exchangeable	2.7	0.9	4.2	0.9	0.5	1.0
Carbonate	3.2	1.1	3.6	7.3	14.3	13.0
Fe-Mn Oxide	16.0	0.8	21.1	34.0	49.3	33.1
Organic/Sulfide	3.7	0.9	27.7	17.3	9.0	36.2
Residual	74.4	96.3	43.4	40.4	27.0	16.7

Note: Mobility and bioavailability decrease in the order exchangeable > bound to carbonate > bound to Fe-Mn oxides > organic matter/sulfide complexes > residual fraction. The organic/sulfide and residual fractions are considered non-bioavailable.

Mercury is the metal of greatest environmental concern in drilling wastes discharged to US waters (Neff, 2002b), and sometimes is found at higher concentrations in drilling mud barite and WBM than in clean marine sediments. Lead is the metal of greatest concern in drilling wastes discharged to the North Sea, because some North Sea drilling mud barite contains high concentrations of easily leached lead. The US EPA (1993) set limits on maximum acceptable concentrations of mercury and cadmium in drilling mud barite in 1993, in an effort to decrease the amounts of metals discharged to the ocean in drilling wastes. Drilling mud barite discharged offshore must contain less than 1 mg/kg (ppm) mercury and 3 ppm cadmium (Table 9). Most drilling mud and cuttings discharged to the Gulf of Mexico since imposition of the ELG contain less than about 0.5 ppm total mercury (Neff, 2002b). Trefry et al. (1986) reported that about 80 percent of the mercury in a low trace metal barite (0.12 ppm Hg), typical of those used in offshore drilling muds, is in the refractory/sulfide phase and the remaining 20 percent is associated with the slightly more mobile monosulfide/oxide phases. Little of the mercury dissolves from drilling mud barite under the redox conditions found in marine sediments, including accumulations of drilling mud and cuttings (Trefry and Smith, 2003).

Dissolved metals concentrations were measured at different levels in the pore water of cores from the Beryl A and Northwest Hutton cuttings piles (Shimmiel & Breuer 2000; Shimmiel et al. 2000; Breuer et al., 2004). Although these piles are composed primarily of OBM and SBM cuttings, metals concentrations, but not redox conditions, in the piles probably resemble those in WBM mud and cuttings accumulations in US waters. The dissolved fraction was defined as that with a particle size less than 0.2 µm and was isolated under anaerobic conditions to prevent redox speciation and redistribution of metals. It should be kept in mind that this fraction may also contain metals adsorbed to dissolved or colloidal organic matter, complexed to inorganic ligands, such as sulphide (Bianchini and Bowles 2002), or to very fine particles. These complexed metals are less bioavailable than those in true solution.

Oxygen concentration decreases to near 0 in the top few mm of the Beryl A and Northwest Hutton OBM/SBM cuttings piles (Shimmiel & Breuer 2000; Shimmiel et al. 2000; Breuer et al., 2004) and most other North Sea cuttings piles (Hartley et al., 2003). Under reducing conditions (low oxygen concentrations in sediment pore water), solid Fe, Mn, and Mo oxides dissolve. This dissolution may be partially inhibited by the alkaline pH of the cuttings pore water. The solid Fe and Mn oxides in oxidized sediment layers are strong adsorbants for metals. When the metal oxides dissolve at low oxygen concentrations, some of the dissolved metals adsorbed to them go into solution. Some of the dissolved metals may leach from the cuttings into the overlying water column where they may precipitate again with Fe and Mn oxides if bottom water is oxygenated. Some of the dissolved metals also may diffuse downward in the cuttings, where they encounter rising sulphide concentrations (from microbial reduction of sulfates) and precipitate. Most of the iron and other metals at depth in cuttings piles are present as insoluble, non-bioavailable metal sulfides.

Dissolved barium concentrations in the North Sea cuttings pile pore water tend to increase with depth in the mud and cuttings accumulation (Shimmield & Breuer 2000; Shimmield et al. 2000; Breuer et al., 2004). The solubility of barium in seawater and marine sediments is controlled by the concentration of reactive sulphate, which is high (about 29 mM) in seawater (Neff 2002a,b). In the presence of normal concentrations of inorganic sulphate, the seawater solubility of barite is 81 µg/L (48 µg/L as Ba) at 20°C (Burton et al., 1968). Sulphate reducing bacteria in suboxic layers of the cuttings pile use dissolved sulphate as an electron acceptor for organic matter biodegradation and, in the process, convert sulphate to sulphide. As the sulphate concentration in cuttings pile pore water decreases, barite becomes more soluble, releasing small amounts of barium into solution. This reaction probably is self-limiting because dissolution of barite releases sulphate into solution. However, if barite concentration in sediments is high, it can serve as a source of reducible sulfate for sulfate reducing bacteria (Ulrich et al., 2003), releasing dissolved Ba into the pore water (Phillips et al., 2001). Much of the Ba released into sediment pore water by the activity of sulfate reducing bacteria diffuses upward to the oxic layers of the sediment or into the overlying water column, where it precipitates with sulfate in the oxygenated water phase (Paytan et al., 2002). Thus, barite is highly persistent in marine sediments containing WBM and cuttings.

4.1.2 Bioavailability of metals from WBM and cuttings accumulations in sediments.

Solid metals and metal salts associated with barite, clay, and cuttings particles are not readily bioaccumulated by animals living in close association the cuttings pile; the metals are not passed efficiently through marine food chains (Neff 1987a; Neff et al. 1989b,c; Leuterman et al. 1997; URS 2002). When accumulated, the metals often are not assimilated into the tissues, but remain in the tissues as insoluble, inert concretions, probably of the original barite particles (Jenkins *et al.* 1989).

Neff et al. (1989b), Leuterman et al. (1997), and Schaanning et al. (2002) evaluated the bioavailability to several species of bottom-living marine animals of several metals in different grades (purities) of drilling mud barite in sediments. Some of the marine animals accumulated small amounts of one or more of arsenic, cadmium, copper, lead, mercury, nickel, and zinc during chronic exposure to the high concentrations of the barites containing the highest concentrations of metals. Lead was the only metal in impure grades of barite that was bioaccumulated to potentially toxic concentrations in tissues of marine animals in the experiments performed by Leuterman et al. (1997). Trefry et al. (1986) showed that some lead is leached into solution from barite in the slightly acid environment of the digestive tract of marine animals. Most US and North Sea barites contain low concentrations of lead (Table 5); barite samples used by Leuterman et al. (1997) contained unusually high lead concentrations.

Correlation analysis of the relative concentrations of the metals in the tissues of the test animals and in the barite samples indicated that most of the metals apparently accumulated were still associated with barite particles, probably in unassimilated solid form in the gut. It is probable that some of the metals apparently bioaccumulated by the marine animals were actually still associated with fine particulate barite or other sediment particles in the gut and gills, as was shown for bivalves exposed to drilling muds discharged offshore California (Jenkins et al. 1989). Marine invertebrates can take up fine particles into epithelial cells by pynocytosis. The metals associated with the particles remain in the particles and are not actually assimilated by the animal. These sorbed, particulate metals are toxicologically inert (Nott and Nicolaidou, 1989, 1990, 1993, 1994). Neff et al. (1989b) and Leuterman et al. (1997) concluded that metals associated with drilling mud barite have a low bioavailability to marine organisms that might come in contact with discharged drilling fluid solids.

Much of the exchangeable metals associated with barite would likely be leached into the water column during settling of a WBM through the water column (Trefry et al., 1986; Neff, 1991). Thus,

concentrations of bioavailable metals in pore water of a sediment containing deposited drilling mud solids probably would be much lower than used in these investigations.

Similar results have been obtained in laboratory studies in which marine animals were exposed to drilling muds in sediments. Neff et al. (1989b) exposed lobsters and flounder for up to 99 days in mesocosm tanks to sediments contaminated with solids from a WBM. Some of the test animals also were fed polychaete worms that had been contaminated by exposure to WBM solids. Concentrations of barium and chromium, the two most abundant metals in most WBM, were measured at different times during the exposure. Lobster and flounder accumulated small amounts of barium, but not chromium, from the contaminated sediments. Flounder, but not lobsters, exposed simultaneously to contaminated sediments and food accumulated slightly more barium than those exposed to contaminated sediments alone. Neither species accumulated chromium from contaminated food. It is probable that much of the barium apparently bioaccumulated by the lobsters and flounder was present as unassimilated barite particles in the digestive system. Chromium, mostly from chrome lignosulfonate, was probably in the low solubility trivalent state and was not very bioavailable. These experiments show that there was very little food chain transfer and no biomagnification of barium and chromium from drilling muds in marine animals.

A joint URS, Dames and Moore, and TNO team (URS, 2002) performed a similar laboratory bioaccumulation experiment with OBM cuttings from two platforms in the North Sea. The results of their studies were similar to those discussed above for WBM and WBM cuttings. The only evidence of a statistically significant metal accumulation by marine animals in OBM cuttings was for lead. The lead concentration was high in the OBM cuttings and its concentration increased in worms, mussels, and turbot during the exposure. None of the benthic marine animals bioaccumulated mercury from the mercury-contaminated drilling mud cuttings. The OBM cuttings contained 0.13-0.19 $\mu\text{g/g}$ dry wt mercury, compared to less than 0.005 $\mu\text{g/g}$ in the reference sediment. These mercury concentrations are typical for drilling muds and cuttings discharged in US and North Sea waters and clean natural sediments, respectively. The results of this study are in agreement with those of Neff et al. (1989b,c), Leutermaier et al. (1997), and Schaanning et al. (2002) that the metals associated with drilling mud ingredients and cuttings have a low bioavailability to marine animals. Lead appears to be the only metal that is bioavailable in some cuttings piles.

During the exposure, turbot (a flatfish) fed on the polychaetes in the mesocosm tanks (URS, 2002). The biomagnification factor (BMF) of the metals by turbot was estimated as the ratio of the concentration in the turbot tissues to the concentration in the food. BMFs ranged from <0.01 to 0.42, indicating that biomagnification was not taking place. These results confirm those of Neff et al. (1989b) that there is little trophic transfer and no biomagnification of metals from drilling mud and cuttings in benthic environments.

Field studies confirm that little or no metals are bioaccumulated from drilling muds and cuttings by benthic marine animals. Attempts to correlate elevated sediment concentrations of barium, occasionally chromium, and rarely zinc, cadmium, lead and mercury near drilling sites with accumulations of metals in tissues of resident benthic or demersal (i.e., bottom-feeding) fauna sometimes demonstrated small increases in barium concentrations in tissues. Bioaccumulation of other metals, particularly mercury, rarely was observed; in most cases where a small increase in metals concentrations was reported in tissues of marine organisms near a platform, review of the data revealed sampling or analytical problems that confounded the validity of the results (National Research Council, 1983; Neff, 1987a; Hinwood et al., 1994)

Because mud- and cuttings-associated metals have a low bioavailability, they do not enter the local food web and do not get passed through the food web to fishery species consumed by man (Neff, 1987a, 2002; Neff et al., 1989b,c). When accumulated in the tissues of sediment-dwelling marine organisms, they

remain in the tissues as insoluble, inert concretions, probably of the original barite particles (Jenkins et al., 1989).

There have been several surveys of the concentrations of metals in tissues of marine animals from the vicinity of offshore platforms (Neff et al., 2000; Neff, 1987a, 2002b). In nearly all cases, these surveys have shown that metals concentrations in tissues of marine animals near platforms are similar to concentrations in tissues of the same or similar species well away from and out of the influence of the platforms. Thus, the metals discharged from platforms in drilling muds and cuttings are diluted rapidly to natural background concentrations or are in forms that are not bioavailable to marine animals.

Cripps *et al.* (1999) reported that mussels (*Mytilus edulis*) collected from the surface of cuttings piles in the Norwegian Sector of the North Sea contained higher concentrations of several metals in soft tissues than mussels from uncontaminated marine areas of the North Sea. The mussels are part of the biofouling community on submerged platform structures and probably became detached from the platform and settled to the bottom on the cuttings piles. The metals in the mussel soft tissues could have come from the metal platform structures to which they had been attached, from produced water or other waste discharges, or from the cuttings piles themselves. Thus, these observations, though suggestive that metals in cuttings piles are somewhat bioavailable, do not provide solid proof of such bioavailability.

Concentrations of barium and chromium, but not other metals were slightly elevated in sediments near exploratory drilling operations on Georges Bank after drilling (Neff et al., 1989a). However, metals concentrations in sea clams *Arctica islandica* collected from surface sediments near the drilling rigs were in the normal range for bivalve mollusks (Phillips et al., 1987). There was no correlation between concentrations of barium in sediments and bivalve tissues. There was sufficient variability in tissue concentrations of other metals that there were no statistically significant differences in tissue concentrations between reference and rig site bivalves.

Mauri et al. (1998) measured concentrations of several metals in tissues of two species of bivalve mollusks, *Mytilus galloprovincialis* and *Corbula gibba*, from platform legs and sediments adjacent to a gas platform in the Adriatic Sea 8 years after completion of drilling. The distribution of lead, copper, and chromium in sediments indicated a probable origin from drilling mud and cuttings discharges. Zinc and aluminum in sediments probably were primarily from sacrificial anodes on platform structures. Bivalves from platform legs and nearby sediments contained higher concentrations of lead, copper, and zinc than bivalves distant from the platform, suggesting metal bioaccumulation from platform sources. The authors identified anodes as the main source of the excess metals in bivalve tissues. Thus, laboratory and field studies are consistent in showing that there is a very limited bioavailability of metals from drilling muds and cuttings to marine animals.

4.1.3 Bioavailability of Organic Ingredients (Mainly Hydrocarbons) from WBM.

Relatively little information is available about the bioavailability of organic compounds from WBM and WBM cuttings. Petroleum hydrocarbons, particularly PAH, are the organic compounds sometimes present in WBM and associated cuttings that pose the greatest risk of bioaccumulation and toxicity. Payne et al. (1984) and Phillips et al. (1987) examined saturated and aromatic hydrocarbons by UV fluorescence and gas chromatography/flame ionization detection in sediments, sea clams *Arctica islandica*, and flounder *Paralichthys oblongus* from the vicinity of exploratory wells on Georges Bank off the New England coast. One of the exploratory rigs had added diesel fuel to WBM to free stuck pipe and had discharged WBM containing approximately 100 L of petroleum hydrocarbons. Concentrations of saturated and aromatic hydrocarbons were low in sediments, clams, and fish. Sediments near the rigs contained less than 1 µg/g total aromatic hydrocarbons (mainly PAH), consistent with background

concentrations in this region (Boehm and Farrington, 1985). There was no evidence that the two benthic/demersal marine animals bioaccumulated any hydrocarbons.

Sjøgren et al. (1989) measured concentrations of several petroleum hydrocarbon classes in livers of Atlantic cod *Gadus morhua* from the immediate vicinity of North Sea platforms discharging WBM and cuttings or OBM cuttings, and compared concentrations to those in cod collected more than 10,000 m from the nearest discharge (Table 15). TPH concentration was similar in livers of fish from all three locations. However, PAH and decalins concentrations were higher in livers of fish from the vicinity of the WBM- and OBM-discharging platforms. Livers of fish from the vicinity of the WBM-discharging platforms contained lower concentrations of PAH and decalins than livers of fish from the vicinity of the OBM-discharging platforms. Alkylcyclohexane concentrations were similar in livers of fish from the WBM-discharging and reference platforms. These results indicate that PAH and decalins (2-ring saturated hydrocarbons), probably from petroleum, are bioavailable from WBM and OBM cuttings accumulations. It is possible that some of the hydrocarbons could have been derived from produced water and other discharges from the platforms. Decalins are abundant in many North Sea produced Waters (Durell et al., 2005).

Table 15. Mean and range (in parentheses) of concentrations ($\mu\text{g/g}$ dry wt) of several hydrocarbon classes in livers of Atlantic cod *Gadus morhua* collected within 250 m of platforms in the Norwegian North Sea that were using and discharging water drilling muds and cuttings (WBM) or oil based drilling muds and cuttings (OBM) and from more than 10,000 m from discharging platforms (Reference). From Sjøgren et al. (1989).

Hydrocarbon Class	WBM	OBM	Reference
THC ^a	978 (820 – 1110)	928 (510 – 1890)	880 (560 – 1170)
NPD ^b	0.40 (0.08 – 0.69)	1.80 (0.44 – 3.2)	0.06 (0.004 – 0.11)
C ₅ -C ₆ Decalins	12.0 (8.3 – 18)	16.4 (1.0 – 65)	5.5 (1.4 – 15)
C ₈ -Alkylcyclohexanes	2.7 (1.7 – 3.6)	6.8 (0.11 – 26)	1.6 (0.4 – 3.1)

^a Total hydrocarbons measured by GC/FID. ^b Polycyclic aromatic hydrocarbons, including naphthalene, phenanthrene/anthracene, and dibenzothiophene and their C₁-C₃ alkyl homologues measured by GC/MS.

4.2 Toxicity of Water Based Drilling Muds to Marine Organisms

4.2.1 Drilling Mud Ingredients.

Requirements for toxicity testing of drilling mud and drilling mud ingredients differ in different regions of the world. Jones et al. (1996) compare toxicity testing for three regions: Russia, the United States, and the North Sea countries. In the U.S., a single organism, *Americamysis [Mysidopsis] bahia*, is used for toxicity tests with dispersions of used whole drilling muds. The North Sea countries test the individual drilling mud components with at least 3 organisms at different taxonomic positions: alga, crustacean, fish. Russian regulations require toxicity testing with several species on individual drilling mud components (Patin, 1999).

Despite concerns regarding different methods used for toxicity testing, WBM have been shown to have little or no toxicity to marine organisms. Although the United States requires testing on whole muds and Russia and the North Sea countries require testing of the individual drilling mud components, the end result for WBM is very similar - they exhibit a low risk of ecologically significant chemical toxicity (Jones, et. al., 1996).

The most abundant chemicals, based on mass, in WBM, other than water, are weighting materials, viscosifiers, various inorganic salts for pH and shale control, and sometimes lost circulation materials (Table 3). These chemicals usually represent more than 90 percent of the mass of additives to the continuous phase of the mud. These WBM chemicals would be classified as non-toxic or practically non-toxic to marine organisms in the revised hazard evaluation scheme (Table 16) developed by the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP, 2002) (Table 17).

Barite. Barite is the most abundant solid ingredient in most WBM. Several marine toxicity tests have been performed with dispersions of barite particles in seawater (barite has a very low solubility in seawater [about 80 µg/L]). Particulate barite is nearly insoluble and is essentially inert toxicologically to marine organisms; most bioassays with marine organisms have produced median lethal concentrations greater than 7,000 mg/L suspended barite (National Research Council, 1983). Barium (as barite) is toxic to embryos of the crab *Cancer anthonyi* at concentrations greater than 1,000 mg/L (Macdonald et al., 1988). This concentration is 20,000 times higher than the aqueous solubility of barium in seawater, so any adverse effects probably are caused by physical effects of fine-grained barite particles.

Table 16. Revised marine water column toxicity classification of GESAMP (2002). Acute toxicities (LC/EC/IC₅₀) and chronic toxicity (no observed effect concentration: NOEC) are given in mg/L (parts per million in water).

Toxicity Rating	Acute Toxicity	Chronic Toxicity
Non-toxic	>1000	>1.0
Practically non-toxic	>100 - ≤1000	>0.1 - ≤1.0
Slightly toxic	>10 - ≤100	>0.01 - ≤0.1
Moderately toxic	>1.0 - ≤10	>0.001 - ≤0.01
Highly toxic	0.1 - ≤1.0	<0.001 (1 part per billion)
Very highly toxic	>0.01 - ≤0.1	---
Extremely toxic	<0.01	---

Table 17. Summary of acute toxicities, measured as median lethal concentration (LC₅₀) after 48 – 96 hours, of WBM ingredients to marine algae and animals, summarized from the scientific literature. Toxicities are expressed as mg/L (ppm) of the ingredient or a suspended particulate phase of the ingredient (for insoluble solids).

WBM Ingredient	Range of LC ₅₀ for different species (mg/L)
Weighting Materials	
Barite (barium sulfate: BaSO ₄)	385 ^a - >100,000
Hematite (iron oxide: Fe ₂ O ₃)	>100,000
Siderite (iron carbonate: FeCO ₃)	>100,000
Viscosifiers	
Bentonite (montmorillonite clay)	9600 ^a - >100,000
Hydroxyethyl cellulose (HEC) polymer/viscosifier	7800 – 29,000
Sodium carboxymethyl cellulose (CMC)	500 ^a - >100,000
Polyanionic cellulose	60,000 – 100,000
Organic polymers	7800 - >100,000
Xanthan gum	420

Table 17. Continued.

WBM Ingredient	Range of LC ₅₀ for different species (mg/L)
Salts for pH and Shale Control	
Potassium chloride (KCl: muriate of potash)	2100 ^b
Lime (CaO)	70 – 450 ^b
Calcite (calcium carbonate: CaCO ₃)	>100,000
Sodium hydroxide (NaOH: caustic soda)	105 – 110 ^b
Lost Circulation Materials	
Mica	>7500
Jellflake® shredded cellophane	>7500
Thinners, Clay Dispersants	
Ferrochrome lignosulfonate	12 – 1500
Chrome lignosulfonate	12200 – 100,000
Chrome-treated lignosulfonate	465 – 12200
Chrome-free lignosulfonate	31,000 – 100,000
Iron lignosulfonate	2100
Modified chrome lignite	20,100
Potassium lignite	>100,000
Carbonox® lignitic material	6500 - >7500
Generic lignite	>15,000
Sulfomethylated tannin	33,900 - >100,000
Sodium acid pyrophosphate (Na ₄ P ₂ O ₇)	870 ^b - >100,000
Lubricants	
Diesel fuel	0.1 - 1112
Fatty acid high pressure lubricant	3500 - >100,000
Blended organic ester lubricant	10,400 – 49,400
Graphite	86,500
Other Additives	
Corrosion inhibitors (several types)	2.0 – 7000
Ammonium bisulfite corrosion inhibitor	75,000
H ₂ S scavengers (zinc salts)	235 – 7800
Low MW polyacrylate reverse breaker	3500
Polyacrylate scale inhibitor	77,300
Scale inhibitors	>10,000
Glutaraldehyde (biocide) (25%)	41 – 465
Flocculant WT-40	5300
Surfactants	40 – 429
Detergents	0.4 – 340
Defoamers	5.4 – 84
Tributyl phosphate surfactant defoamer	5100
Emulsion breakers	3.6 - 930
Oxygen scavenger (sodium bisulfite)	175 – 185

^a Microalga test; effects probably caused by turbidity. ^b Freshwater species used in test; salt water species expected to be much more tolerant because of high ionic strength and buffer capacity of seawater.

The toxic responses from barite are due to physical interactions with gills, the gastrointestinal tract, and integument, as opposed to chemical toxicity. In several chronic studies with shrimp *Palaemonetes pugio*

and substrates heavily contaminated with solid barite, barium, as barite, accumulated in the exoskeleton, hepatopancreas, and muscle tissue. In addition, barite ingestion caused damage to epithelial tissue of the gut. Barite mixed with sediments or as a layer on the sediment surface interfered with but did not prevent recruitment of several planktonic larvae of polychaetes and mussels to sediments (Tagatz and Tobia, 1978). No adverse effects were observed in the polychaete worm *Mediomastus ambiseta* on fecal production, growth, and tube production of adults living in barite-covered sediments. These polychaetes migrate out of patches of 100% barite (Starczak, et. al. 1992). Tagatz and Tobia (1978) found that fewer individuals and species colonized sediments covered by a thin layer of barite compared to control sediments.

Cranford et al. (1999) exposed juvenile sea scallops, *Placopecten magellanicus*, to suspensions of 0.5 and 2.5 mg/L (ppm) barite in a flowing seawater system for 28 days. Survival at both doses was similar to that among controls. However, scallops exposed to both barite concentrations had lower gonad growth than control scallops did and, at the higher dose, digestive gland weight was significantly different from control. Control water was unfiltered Bedford Basin sea water that probably contained much lower natural suspended matter concentrations than benthic boundary layer water (water at the sediment/water interface) on Georges Bank where the scallops were obtained (Parmenter et al., 1983), possibly affecting the results of this study of effects of suspended particulate matter on scallops.

Barite in water based drilling mud apparently affected the scallops less than pure solid barite did. Acute and chronic exposure of scallops to 100 mg/L water based drilling mud had no significant effect on survivorship or growth (Cranford et al., 1998). It is probable that concentrations of suspended barite, clay, or drilling mud particles increased in the exposure water during the chronic flow-through toxicity tests, so the scallops were actually exposed to higher than the nominal suspended solids concentration late in the test when most effects were observed. The effects of barite were similar to those of bentonite clay and probably were caused by physical damage to delicate gill epithelial membranes and interference of the suspended particles with feeding efficiency in this active filter-feeding mollusk. Au et al. (2004) reported that chronic exposure to suspended sediments at concentrations frequently found in estuarine environments cause gill damage in juvenile grouper (a fish).

Clams *Cerastoderma edule* that were exposed to 1-3 mm of a barite mud mixture for 12 days experienced coagulated and shortened cilia. In some extreme cases the gill structure disintegrated, probably caused by clogging and abrasion by the fine barite particles. There was 100% mortality within 12 days (Barlow & Kingston, 2001).

Bivalve mollusks use intracellular digestion in the epithelial cells of the digestive gland to deal with particulate foods. It is possible that, during chronic exposure, the fine particles of barite, bentonite, or whole drilling mud accumulate in digestive vacuoles in the digestive gland epithelium to concentrations that interfere with normal digestion. Gill and mantle epithelia also can physically accumulate fine particles by pinocytosis (formation of intracellular vacuoles), possibly explaining the damage sometimes observed in these tissues following exposure to suspended inorganic particles.

Bentonite. Bentonite (sodium montmorillonite clay) is naturally occurring, insoluble clay that usually is considered non-toxic. It is added to drilling muds in quantities ranging from 30-140 kg/m³ (1-50 pounds/barrel) to provide viscosity to suspend barite and cuttings, as well as for filtration control (Table 1).

Bentonite is non-toxic in many 96-hr acute toxicity studies with LC₅₀s ranging from 22,000- >100,000 ppm for various organisms (Table 17). Studies show that bentonite is only toxic for the first few hours of exposure, while the clay-sized solids were in suspension. Once the clay settles to the bottom, no further effects are observed (Carls and Rice, 1984). However, chronic exposure to bentonite suspensions can

bury bottom-living organisms in clay, causing chronic mortality. Oysters that were exposed to as little as 100 ppm suspended bentonite for 192 days suffered elevated mortalities, probably through burial and clogging of the gills (Cabrera, 1971).

Toxic responses that occur as a result of physical harm include abrasion, erosion, or clogging of respiratory surfaces (Sprague and Logan, 1979). Suspended bentonite is toxic to microalgae, *Skeletonema costatum*, at levels of 9600 ppm. This effect can be attributed to the shading effect of the bentonite clay suspension, reducing the penetration of sunlight into the water, reducing photosynthesis in the alga.

Bentonite has been supplemented or replaced by organic polymers as viscosifiers in many modern WBM. Carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), and guar gum are examples of carbohydrate polymers used as viscosifiers in WBM. They have poor thermal stability and so usually are used mainly in shallow parts of a well. They also are highly biodegradable and, therefore, require a biocide. Glutaraldehyde is the biocide used most frequently today. The carbohydrate viscosifiers, like bentonite, are considered non-toxic to aquatic organisms (Table 17). Xanthan gum is practically non-toxic to trout (Sprague and Logan, 1979).

Biocides. Glutaraldehyde is a liquid derivative of glutaric acid; it is added to WBM as a biocide to control bacterial growth, particularly when the mud formulation includes large amounts of biodegradable carbohydrate polymers. Although it is used in small doses, 0.2-1.0 kg/m³, it is toxic. However, it is destroyed rapidly by biological degradation and reduction by oxidation of organic matter when discharged to the marine environment. If used in large excess in a polymer mud, sufficient glutaraldehyde could persist long enough in the mud/cuttings plume to be toxic to pelagic organisms.

Glutaraldehyde is moderately toxic to non-toxic to various freshwater and marine animals with LC₅₀s ranging from >6-2200 ppm for several crustaceans (Table 17). As a biocide, glutaraldehyde is less toxic than other products used in the past, such as Dowacide G® & Dowacide B®, that have LC₅₀s less than 1 ppm.

Inorganic Salts. Some of the salts added to WBM for alkalinity/pH or shale control are slightly toxic to freshwater plants and animals (Table 17). Toxic effects in these species are caused by ionic or pH effects. Because of the high ionic strength and buffer capacity of seawater, it is unlikely that these inorganic salts would be toxic to marine organisms at the concentrations at which they occur in WBM.

Thinners and Clay Dispersants. Lignosulfonate is an organic salt that is produced as a by-product of the sulfite process for separation of cellulose pulp from wood (Hudgins, 1991). Some chrome and ferrochrome lignosulfonate thinners are slightly toxic to marine organisms (Table 17). Because of concern about their possible environmental impacts, many offshore operators have replaced the chrome lignosulfonates with less toxic chrome-free lignosulfonate salts. Other clay thinners, such as lignites and tannins, are not toxic (Table 17).

4.2.2 Acute Toxicity of Whole WBM.

Many laboratory toxicity tests have been performed since the mid 1970s on the acute and chronic toxicity of WBM to freshwater and marine animals. By 1983, 62 species of marine animals from the Atlantic and Pacific Oceans, the Gulf of Mexico, and the Beaufort Sea had been tested in 400 bioassays with 72 different WBM (National Research Council, 1983). Nearly 80 percent of the median lethal concentrations (96-h LC₅₀) were greater than 10,000 mg/L (ppm) drilling fluid, considered non-toxic by the GESAMP toxicity classification (Table 16).

Subsequently, 8 generic WBM, representative of the types of drilling fluids used offshore in US waters, were identified and characterized chemically and toxicologically (Ayers et al., 1983). The mysid (*Americamysis [Mysidopsis] bahia*), a small shrimp-like crustacean, was identified as one of the most sensitive species to drilling fluids and a suspended particulate phase preparation was recommended as the best simulation of the type of drilling fluid dispersion encountered by water column organisms (Neff et al., 1980). Bioassays performed by the U.S. EPA (1985a,b) with the suspended particulate phase of 8 generic muds and mysids gave 96-h LC₅₀s ranging from 3,300 mg/L to >100,000 mg/L mud added (Duke et al., 1984) (Table 18), similar to results obtained by Ayers et al. (1983). A KCl-polymer mud had the lowest LC₅₀, still within the non-toxic range. The results of these tests were used by EPA to set an acute toxicity (LC₅₀) limit for water based drilling muds of 3,000 ppm drilling mud added (30,000 ppm suspended particulate phase) in the current ELG..

Table 18. Acute Toxicity of the suspended particulate phase (SPP) of 8 generic drilling muds to mysids. 96-hour LC₅₀ Concentrations are mg/L mud added. From Duke et al., (1984).

Drilling Mud Type	96-Hour LC ₅₀
KCl Polymer Mud	3,300
Seawater Lignosulfonate Mud	62,100
Lime Mud	20,300
Non-Dispersed Mud	>100,000
Seawater Spud Mud	>100,000
Seawater/Freshwater Gel Mud	>100,000
Lightly Treated Lignosulfonate Mud	68,200
Freshwater Lignosulfonate Mud	30,000

All US offshore operators are required by the NPDES permit to perform suspended particulate phase bioassays on used drilling fluids each month during drilling and at the end of the well. Data collected by EPA between 1986 and 1989 showed that 99.9 percent of 10,397 Gulf of Mexico drilling mud bioassays yielded a 96-h LC₅₀ in excess of the 30,000 ppm suspended particulate phase limit (SAIC, 1992). Thus, the vast majority of water based drilling muds used offshore in U.S. waters are not toxic to marine organisms.

4.2.3 Causes of WBM Toxicity.

As expected from the low toxicity of whole used WBM, the toxicity of most individual drilling mud ingredients also is low (Table 17). Of the major drilling mud ingredients, only chrome- or ferrochrome-lignosulfonate may be moderately toxic to marine animals (Neff, 1987a; Parrish et al., 1989). The most toxic minor (based on volumes discharged) additives sometimes used in WBM include diesel fuel, biocides, corrosion inhibitors, detergents, defoamers, and emulsion breakers (Table 17). The metals sometimes associated with impure barite and bentonite in WBM probably do not contribute to drilling mud toxicity, because of their low bioavailability (Schaanning et al., 2002), as discussed above.

Conklin et al. (1983) showed that the toxicity of a whole drilling mud could be attributed primarily to chrome only when chromate plus chrome lignosulfonate concentrations in the mud were very high. Several minor additives, such as zinc-based H₂S scavengers, tributyl phosphate surfactant defoamer, and fatty acid high temperature lubricant are toxic, but usually are not present in used drilling fluids at concentrations high enough to contribute significantly to whole mud toxicity.

The acute toxicity of WBM containing petroleum additives increases as hydrocarbon concentration increases. Conklin et al. (1983) observed a statistically significant inverse relationship between the

toxicity to estuarine shrimp of 18 samples of WBM from a coastal drill site in Alabama and the concentrations in the WBM of diesel fuel (the drilling fluids contained between 170 and 8,040 ppm total petroleum hydrocarbons) (Figure 8). Breteler et al. (1988) showed that petroleum additives increased the toxicity of WBM to water column and benthic marine animals. Drilling fluids containing a high-sulfur diesel fuel (containing 25 % total aromatic hydrocarbons) were the most toxic, followed closely by drilling fluids containing a low-sulfur diesel (containing 8.7 % total aromatics); drilling fluids containing a low-aromatic mineral oil were the least toxic.

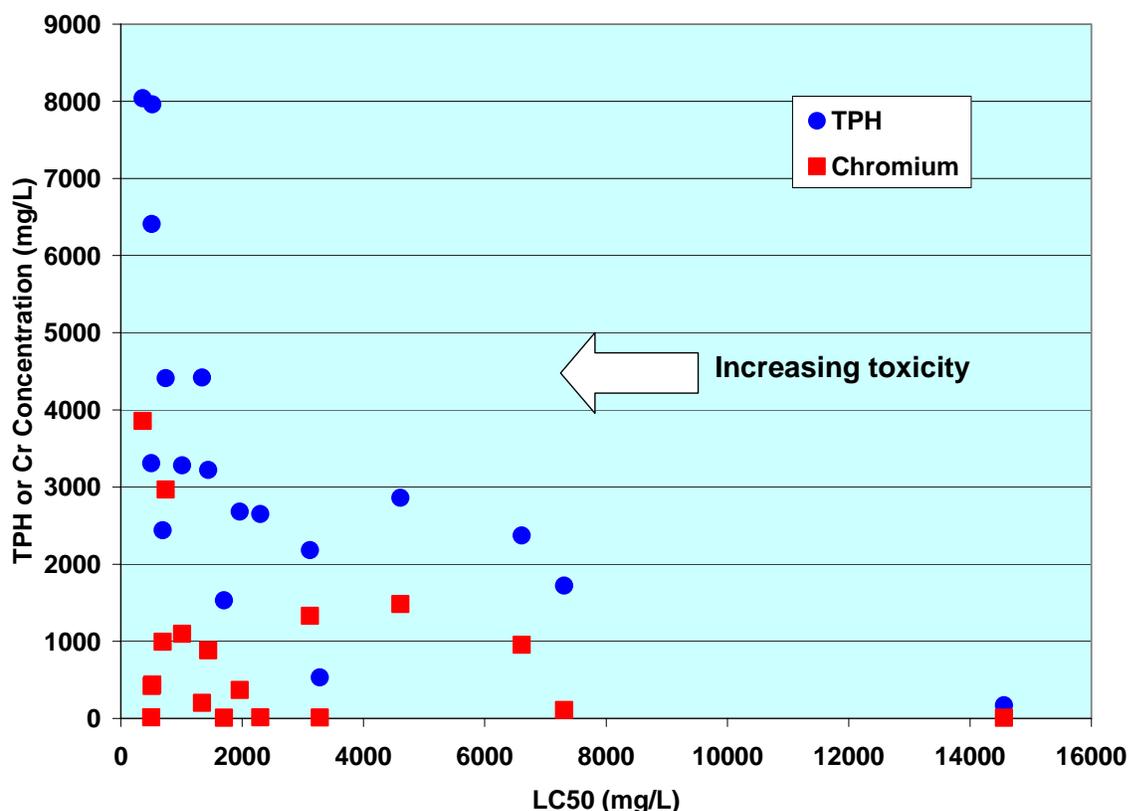


Figure 8. Relationship between the toxicity to grass shrimp of water based drilling fluids collected at 18 depths in a Mobil Bay, AL, well and concentrations of chromium and total petroleum hydrocarbons (TPH) in the muds. From Conklin et al. (1983).

4.2.4 Chronic and Sublethal Effects of WBM.

Although acute studies are the most widely used and commonly accepted way of determining toxicity, chronic studies for sub-lethal effects often are a better predictor than acute studies of potential population- and ecosystem-level effects. Chronic studies more closely simulate exposure concentrations, durations, and conditions in the field.

The most toxic WBM used offshore in the U.S, chrome and ferrochrome lignosulfonate muds, were evaluated extensively for sublethal effects in the 1970s and 1980s (National Research Council, 1983; Neff, 1987a). The effects of various lignosulfonate muds include alterations in feeding behavior of lobsters; cessation of swimming by crab and mysid larvae, inhibition of shell formation, reduced rate of shell regeneration, and damage to gills in various mollusks,; reduction in calcification, respiration, and

growth rates of several corals; and a decrease in growth rate, depressed heart rate, developmental abnormalities, and reduced survival of several species of marine fish. It is uncertain if these effects would be manifested under conditions of exposure to drilling muds and cuttings that occur in the field. Field studies near ocean discharges of WBM and cuttings generally do not give evidence of long-lasting ecological impacts.

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5.0 FIELD STUDIES

Given the wide dispersal of dissolved and solid components of WBM and cuttings discharges to the ocean, and the low toxicity of WBM that do not contain high concentrations of petroleum products, one would expect that impacts of these discharges on the water column and benthic environment would be minimal and of short duration. Many field monitoring studies, most in the U.S. Gulf of Mexico and the North Sea, have been performed since the 1970s to determine short- and long-term impacts of drilling discharges on the marine environment. Most of the monitoring in the North Sea has focused on impacts of OBM cuttings and, more recently, SBM cuttings discharges. Olsgard and Gray (1995) reviewed the North Sea monitoring data and concluded that “preliminary results from fields using only WBM clearly indicate a reduction in environmental contamination and biological impact, compared to effects reported here for OBM drill cuttings.” The authors suggested that the lesser effects of the WBM and cuttings than OBM cuttings indicated that the main adverse effects of OBM cuttings are caused primarily by the oil components in the mud adhering to the cuttings.

Earlier, a study panel of the U.S. National Research Council (1983) examined all the information available at that time on the environmental fates and effects of WBM and cuttings discharges and concluded:

“Based on laboratory and field studies to date, most water-based drilling fluids used on the U.S. OCS have low acute and chronic toxicities to marine organisms, (because of) the expected or observed rates of dilution and dispersal of drilling muds in the ocean after discharge. Their effects are restricted primarily to the ocean floor in the immediate vicinity and for a short distance downcurrent from the discharge. The bioaccumulation of metals from drilling fluids appears to be restricted to barium and chromium and is observed to be small in the field.”

More recent laboratory and field studies have tended to confirm these conclusions. Water column communities apparently are not harmed by drilling mud and cuttings discharges, because discharges are intermittent and of short duration during drilling and dispersion and dilution is rapid of dissolved and particulate components of the discharge. Aldredge et al. (1986) could not detect significant biological effects of WBM and WBM chemicals on phytoplankton communities from the Santa Barbara Channel, California.

As a general rule, effects of WBM and cuttings discharges on the benthic environment are related to the total mass of drilling solids discharged and the relative energy of the water column and benthic boundary layer at the discharge site. In high energy environments, such as Cook Inlet, Alaska, (Lees and Houghton, 1980; Houghton et al., 1980a), and Georges Bank off the New England coast (Bothner et al., 1985; Neff et al., 1989a), little drilling waste accumulates on the sea floor and adverse effects of the discharges can not be detected.

There were small increases in concentrations of barium and chromium in the fine-grained fraction of sediment near exploratory rigs on Georges Bank during and for a short time after drilling (Bothner et al., 1985; Neff et al., 1989a). Approximately 9200 metric tons of drill cuttings and 5000 metric tons of WBM solids were discharged from the 8 exploratory wells drilled on Georges Bank between 1981 and 1982 (Neff, 1987b). Some of the WBM contained diesel fuel (Phillips et al., 1987). The benthic fauna were abundant and diverse throughout the study area during the 3 years of the study. Some species showed large seasonal fluctuations in abundance, probably due to disturbance of the bottom by severe winter storms. However, no changes were detected in benthic communities of Georges Bank that could be attributed to drilling activities.

Similar results were obtained in a four-year study of the effects of drilling discharges from 3 offshore platforms on soft-bottom and hard-bottom benthic communities on the continental shelf off Point Arguello, California (Hyland et al., 1994). During the study, a total of 39 wells were drilled and more than 11,000 metric tons of drilling muds, including 5,000 metric tons of barite, were discharged from the 3 platforms. No effects were observed in the soft bottom benthic community. Responses of the hard bottom communities inhabiting rocky outcrops were highly variable, probably representing both seasonal and environmentally-induced changes. Abundances of some species increased and abundances of some others decreased during the period of drilling waste discharges. Changes in populations of only a non-reef-forming coral and a galatheid crab appeared to be correlated with drilling discharges. The effects on the hard bottom community, if they occurred, were not due to chemical toxicity of drilling mud solids. They probably were caused by physical effects of elevated suspended particle concentrations. The authors predicted that recovery from such physical effects probably would begin as soon as drilling mud and cuttings discharges ceased.

Daan and Mulder (1993, 1996) studied the effects of WBM discharges from a platform in the Dutch Sector of the North Sea. Ecological surveys performed 2 months and 1 year after completion of drilling revealed no measurable adverse effects on the benthic community, even at stations as close as 25 m from the discharge. At both sampling times, there was no significant spatial trend in the number of benthic species and their abundance along a transect extending from 25 m to 5000 m down-current from the WBM discharge. Only small amounts of mud and cuttings solids were detected in sediments near the platform, suggesting that the discharged solids were transported away from the site and diluted to non-detectable concentrations within 2 months after completion of drilling.

Similar results were obtained in a monitoring study of benthic impacts of exploratory drilling and WBM discharge in the Minerva gas field in 60 m of water off the south coast of Victoria, Australia (Currie and Isaacs, 2005). Benthic community structure in sediments collected along transects from the wellhead to 6400 m was studied shortly before and for up to 11 month after drilling of an exploratory well. Drill cuttings were detected in sediment grab samples and in video surveys by remotely operated vehicle (ROV) within 100 m of the drilling rig shortly after drilling. Drill cuttings were observed in some grab samples collected four months after drilling but not in any samples collected after 11 months. Immediately after drilling, the abundance of benthic fauna and faunal diversity decreased by 45 to 75 percent in sediments within about 100 m of the discharge. Most faunal changes were no longer detectable after four months. However, modified benthic communities persisted for at least 11 months after completion of drilling at stations close to the rig. Thus, impacts of the WBM and cuttings discharges were localized within about 100 m of the discharge and benthic ecosystem recovery was well advanced in less than one year.

Effects of WBM and cuttings discharges on benthic ecosystems sometimes are more severe and long-lasting if the discharges are to low-energy, deep-water environments, shallow coastal waters, or if mud and cuttings are shunted to the bottom. Benthic surveys were performed immediately before and after and 1 year after exploratory drilling on the mid-Atlantic outer continental shelf in 120 m of water (Maurer et al., 1981; EG&G, Environmental Consultants, 1982; Gillmor et al., 1985). Approximately 2160 metric tons of WBM and cuttings were discharged. The benthic boundary layer at the site was low-energy, as indicated by visible evidence of an anchor scour marks and a cuttings pile of clay-sized particles 1 year after completion of drilling. Immediately after drilling, there was a 150-m diameter zone of visible clay-sized cuttings accumulation, up to 1 m deep, just south of the drilling site. Elevated concentrations of clays were detected up to 800 m from the discharge site.

The abundance of certain large, motile predatory species, such as fish, crabs, and starfish, increased near the rig site between the pre-drilling and first post-drilling surveys. These animals probably were attracted

to the area by the increased bottom-relief afforded by the cuttings pile, or by the clumps of mussels and other biofouling organisms that had fallen off the drilling rig or anchor chains. The abundance of these animals decreased in the year after drilling.

There apparently was a nearly four-fold decrease between the pre-drilling and first post-drilling surveys in the abundance of animals living in sediments (benthic infauna) near the discharge site. This decline in abundance was the same for the four major taxonomic groups (polychaetes, echinoderms, crustaceans, and mollusks). Although the abundance of polychaetes declined, the composition of polychaete feeding guilds remained essentially unchanged. These declines persisted, but with decreasing severity, for at least 1 year and, because they were correlated with elevated concentrations of clay in sediments, probably were caused by burial and changes in sediment texture by accumulation of drill cuttings. There was evidence of some ecological recovery in the year after completion of drilling.

There also was evidence of drilling solids accumulations and benthic ecological impacts around a platform 22 km off the Texas coast in 24 m of water in the Gulf of Mexico (CSA, 1989; Chapman et al., 1991; Carr et al., 1996). Six wells were drilled from the platform and nearly 20,000 metric tons of WBM, including 17,000 tons of barite, were discharged during 3 years of drilling. An additional 4 exploratory wells were drilled within the lease block. Mean sediment grain size tended to decrease with distance from the platform, suggesting an accumulation of coarse cuttings particles or produced sand. There also were gradients of decreasing concentrations of barium, chromium, cadmium, mercury, and zinc in sediments with distance from the platform.

The benthic macrofaunal community in sediments near the platform was not markedly different from that at reference stations away from the platform. The number of taxa of benthic invertebrates was comparable and the species diversity was greater in sediments within 75 m of the platform than in sediments farther away. Cluster analysis revealed that the benthic community within 75 m of the platform was different from that farther away. Biofouling organisms falling from submerged platform structures formed a shelly sand substrate that supported a unique benthic community.

Chapman et al. (1991) and Carr et al. (1996) reported that some sediments near the platform were toxic to benthic organisms in laboratory tests. However, they also observed that the benthic fauna were relatively uniform and diverse throughout the area, showing little or no effects of the drilling discharge accumulations. Thus, the changes in benthic community structure in sediments near the platform were not caused by toxicity of drilling discharge solids at this shallow-water site.

Although effects on the benthos of the widely dispersed solids resulting from a sea surface discharge of WBM and cuttings usually are minor and ecosystem recovery is rapid (CSA and Barry Vittor & Associates, 1989; Neff et al., 1989a; Hyland et al., 1994), direct shunting of mud and cuttings to near the bottom may cause chronic ecological damage to a small area of the sea floor where solids accumulate in a cuttings pile, mostly from burial of benthic fauna or change in sediment texture. Recovery may be slower if the cuttings pile contains a high organic matter concentration and becomes hypoxic.

Biodegradable organic matter often has a greater effect than sediment texture and deposition rate or, in some cases, chemical toxicity on the structure and function of benthic biological communities in accumulations of drilling muds and cuttings (cuttings piles) on the sea floor (Hartley et al., 2003). Bacteria and fungi living in marine sediments degrade the organic matter and, in the process, may deplete the oxygen in the pore water of near-surface layers of sediment and generate potentially toxic concentrations of sulfide and ammonia (Wang and Chapman, 1999; Gray et al., 2002; Wu, 2002). Sediments containing high concentrations of biodegradable organic matter, particularly if they are fine-grained, often are hypoxic or anoxic and have markedly altered benthic communities compared to nearby oxygenated sediments (Figure 4). As the organic matter concentration decreases as a result of microbial

degradation, the oxygen concentration in the surface layers of sediments increases, resulting in succession in the benthic community structure toward a more stable state. This process is called organic enrichment and results in substantial changes in sediment physical/chemical properties and in benthic community structure (Pearson and Rosenberg, 1978). The depth in sediments of oxygen penetration and the redox potential discontinuity (RPD) increase and the number of species, faunal abundance, and biomass (the SAB ratio) of the benthic community change in characteristic ways along a gradient of decreasing sediment organic matter concentration with distance from a source of sediment organic enrichment, such as a sewage outfall or a platform discharging drilling mud/cuttings, as described in the Pearson-Rosenberg model (Nilsson and Rosenberg, 2000). The changes in the benthic community are caused primarily by sediment hypoxia, rather than directly by organic enrichment or sediment toxicity (Gray et al., 2002).

WBM cuttings piles usually contain low concentrations of biodegradable organic matter and do not support large populations of bacteria (Dow et al., 1990). Dow et al. (1990) layered WBM or OBM cuttings on natural sediments in mesocosms. There was only a slight and short-term reduction in the RPD depth in sediments containing WBM cuttings, whereas in sediments containing OBM cuttings, RPD depth decreased to near the sediment surface and did not return to normal in 1 year. Anoxic conditions in the OBM cuttings accumulation stimulated production of hydrogen sulphide by anaerobic sulphate-reducing bacteria.

Aerobic and sulphate reducing (anaerobic) bacteria in a WBM cuttings accumulation can use carbohydrates (starch, CMC) and acetate from WBM solids as an organic carbon source. Most of the organic chemicals in WBMs are biodegradable under aerobic conditions (Table 19). However, organic chemicals in settled solids from mineral oil- and diesel fuel-contaminated WBM solids containing 2,000 to 7,000 mg/kg total organic carbon have a high COD and BOD (Breteler *et al.* 1988). Thus, WBM cuttings piles contaminated with petroleum hydrocarbons and highly biodegradable carbohydrates may experience the ecological effects of organic enrichment, particularly if the cuttings pile is large.

Table 19. Rates of microbial biodegradation of several organic components of WBMs used in the Mediterranean Sea. Degradation rates were measured as chemical oxygen demand (COD) and 28-day biological oxygen demand (BOD). From Terzaghi et al. (1998).

Chemical Product	COD (mg O ₂ /mg OC)	BOD (mg O ₂ /mg OC)	% Degraded in 28 Days
Lignosulphonate	0.92	0.25	27
Modified starch	0.73	0.53	73
Soltex	0.67	0.09	14
XC-polymer	0.83	0.36	43
Mor-Rex	0.99	1.13	>100
Carboxymethylcellulose	0.75	0.50	50
PAC	0.75	0.21	21
Detergent	0.24	0.12	83
Defoamer	3.39	1.08	32
Sodium acetate	0.57	0.72	92

If drilling mud and cuttings are shunted to and discharged near the sea floor, a large cuttings pile may be produced particularly near a multi-well platform. Shunting is used regularly in the North Sea for disposal of OBM and SBM cuttings, and cuttings piles often are several meters high (Hartley et al., 2003). EPA has required shunting of mud and cuttings on occasion in the Gulf of Mexico, usually to protect nearby

hard-bottom and reef communities from burial and suspended solids effects. This strategy has been effective in protecting the Flower Gardens Banks in the western Gulf of Mexico (CSA, 1985).

The 2-year Gulf of Mexico Offshore Operations Monitoring Experiment (GOOMEX) was designed to determine the effects of long-term gas/condensate development and production activities on the benthic environment near 3 platforms in the western Gulf of Mexico, 2 of which shunted mud and cuttings to the bottom (Kennicutt et al., 1996b). The platforms surveyed include:

- Matagorda Island Area Block 686 (MAI-868) is in approximately 30 m of water; 12 wells drilled (no shunting);
- Mustang Island Area Block A85 (MU-A85) is in about 75 m of water near Baker Bank; 18 wells drilled (shunting);
- High Island A389 (HI-A389) is in about 130 m of water near the East Flower Garden Bank; 6 wells drilled (shunting).

Because of the long elapsed time between the most recent drilling activities and mud/cuttings discharges and the start of the GOOMEX program, and the more or less continuous discharge of produced water and other waste effluents from the platforms during and after completion of drilling, it may not be possible to distinguish among environmental impacts caused by drilling mud and cuttings discharges on the one hand and other discharges and natural environmental variation on the other. Clear evidence of petroleum hydrocarbon contamination in sediments near MU-A85 and HI-A389, the 2 platforms where cuttings were shunted, is highly suggestive of contamination from discharge of oil-contaminated cuttings, accidental oil releases, discharge of produced sand, or discharge of produced water. OBM were used a few times at HI-A389, but presumably were barged to shore for disposal. The three sites were selected because of the high level of sediment contamination. Therefore, impacts on the benthic ecosystem near the platforms can not be attributed exclusively or even primarily to drilling mud and cuttings discharges alone.

Percent sand and total organic carbon (TOC) in surficial sediments decreased with distance from all three platforms (Table 10) (Kennicutt et al., 1996a). The concentration of silt also was elevated in sediments within 50 m of the deepest platform, HI-A389. Mineralogical analysis of the sand indicated that some of it was drill cuttings deposited during drilling from the platforms. Additional enrichment of sand in sediments near the platforms could have come from produced sand discharges (now generally prohibited) and the effects of the platform structure itself on bottom currents and scouring. The authors also suggested that some of the sand may have come from sand-blasting of platform structures to remove paint and rust.

Some sediment samples near platform HI-A389 contained as much as 40 % barite (280 g/kg Ba), a major ingredient of drilling mud (Table 11). Some sediments near platform MU-A85 contained nearly 3 % barium. The high concentrations of barium in sediments near MU-A85 and HI-A389 probably were due to shunting of drilling muds to the sea floor and the high persistence of insoluble barite in low-energy benthic environments.

Sediments collected near the three platforms were lightly contaminated with petroleum hydrocarbons (Table 11). Sediments at most stations contained less than 150 µg/kg dry wt (parts per billion: ppb) total polycyclic aromatic hydrocarbons (PAHs). The highest measured concentration of total PAHs was 6358 ppb in sediments from the vicinity of MU-A85. The unresolved complex mixture of hydrocarbons (UCM) in the sediments rarely exceeded 10 mg/kg (parts per million: ppm). In general, hydrocarbon concentrations in sediments reached background levels within 100 to 200 m of the platforms. Sediments from a few stations near MAI-686 contained small amounts of fresh petroleum resembling a condensate. These hydrocarbons may have been from a pipeline leak or a seep.

Several metals were analyzed in sediment samples (Ag, Al, As, Ba, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, Sn, V, Zn). Total metals concentrations in sediments were highest at HI-A389, intermediate at MU-A85, and lowest at MAI-686, the same order as total hydrocarbons concentrations. Concentrations of barium, cadmium, lead, and zinc were highest in sediments near the platforms and decreased with distance from the platforms. Concentrations of aluminum, chromium (occasionally), iron, nickel, and vanadium showed the opposite trend; concentrations in sediments decreased with proximity to the platforms. There were no clear gradients of concentrations of silver, arsenic, copper, mercury, antimony, selenium, and tin in sediments. However, concentrations of silver, arsenic, and mercury were elevated in some sediment samples collected near HI-A389. A few sediment samples within about 35 m of the shunt pipe at HI-A389 contained more than 2 mg/kg total mercury (Figure 7). This mercury probably came from drilling muds discharged before the limit on mercury in barite became effective or from sand-blasting grit and paint from platform maintenance repainting. Mercury concentrations as high as those in sediments near HI-A389 have never been observed in sediments near other platforms in the Gulf of Mexico (Neff, 2002b).

Metal enrichment in sediments near the platforms was present in only the upper 10 to 15 cm of sediments; the thickness of the metals-enriched layer decreased with distance from the platforms. Elevated hydrocarbon concentrations usually were restricted to the top 2 cm of the sediments near platforms. Barium maxima in sediments near MAI-686 and MU-A85 were below the sediment surface. The authors assumed that the metals and perhaps some of the hydrocarbons were derived from drilling mud and cuttings discharges; However, other sources, particularly produced water discharges, also may have contributed to metals concentrations in sediments.

The tight correlations among barium, cadmium, and mercury concentrations in sediments near platforms is strong circumstantial evidence that cadmium and mercury were present as sulfide impurities in drilling mud barite. There was a lesser correlation between concentrations of barium and lead and zinc in the sediments, indicating that some of the lead and zinc may have come from another source than drilling mud barite, possibly paint chips from the platform, produced water, or drilling mud ingredients other than barite (Neff et al., 1987).

Evidence from earlier field studies near MAI-686 and HI-A389 indicate a substantial decrease in the metals contamination of sediments with time near the shallow-water platform, MAI-686. However, there was little evidence of a decrease with time in metals concentrations in sediments near the deeper-water platform (HI-A389) where drilling muds and cuttings were shunted to 10 m above the bottom in a low-energy environment.

Montagna and Li (1997) used a time dynamic model to simulate effects of sediment contamination near the three platforms on the bioenergetics of the deposit-feeding nematode community in sediments. Production efficiency (production/assimilation x 100%) of deposit-feeding nematodes decreased from about 30 percent in unaffected sediments to less than 15 percent in sediments 50 to 100 m from the platforms. Nematode communities were different in sediments near the three platforms, probably due to differences in natural environmental parameters. It is uncertain if the reduced production efficiency observed in nematodes from sediments near the platforms was due to differences in sediment grain size, or to sediment contamination with zinc (the metal used as an indicator of sediment contamination), or other chemicals. Changes in benthic community composition and function with distance from the platforms could also have been caused by organic enrichment. Some sediments near platforms were enriched in organic matter and were hypoxic (as indicated by Eh values below 0 mV) (Table 11).

Effects of the platforms and their discharges on meiofaunal and macrofaunal communities in surficial sediments were very localized to about 100 m from the three platforms (Montagna and Harper, 1996). The abundance of total polychaetes and nonselective deposit-feeding nematodes in sediments was higher

near the platforms than at stations farther away. However, the abundance and diversity of amphipods and harpacticoid copepods and reproductive success of harpacticoids were lower in sediments near the platforms than at stations farther away. These effects probably were caused by organic enrichment of sediments near the platforms from organic matter deposited from the biofouling community on submerged platform structures, alterations in sediment grain size near the platforms, or sediment contamination with organic fractions of drilling discharges. The authors suggested that the increased abundance of polychaetes and nematodes in sediments near the platforms was due to organic enrichment, whereas the decline in abundance of amphipods and harpacticoids was due to chemical toxicity. However, other studies near production platforms in shallow waters of the western Gulf of Mexico have shown that sediment grain size is the major factor controlling the distribution and abundance of benthic fauna in sediments near platforms (Neff et al., 1992). In any event, effects of the platforms themselves and discharges, including WBM and cuttings, from them on benthic fauna were minor and highly localized near platforms that had been in place for up to 15 years and from which 6 to 18 wells had been drilled. Produced water discharges from the platforms ranged from 10,000 to 100,000 bbl/month (53,000 to 530,000 L/d).

Ellis et al. (1996) compared the abundance and size class structure of macroepifaunal invertebrates (shrimp, crabs, scallops, and starfish) at 50 to 100 m and 3000 m from the three platforms during two seasons in 1993 and 1994. The animals collected by otter trawl were similar at the two shallow water platforms, MAI-686 and MU-A85 and different from the fauna at the deep-water platform, HI-A389. There were few significant differences in catch per unit effort (CPUE) between near- and far-field stations at a platform. The species that were most abundant at near-field or far-field stations were different for each platform. Similar results were obtained for size frequency distributions at near- and far-field stations at the three platforms. The differences could not be explained by diurnal variations in activity (and therefore catchability) of the mobile epifauna or to sex-related differences in size of the animals.

Although the authors attributed these distributions to the unique chemical and physical environment at each platform, it is unclear if chemical contamination of sediments near the platforms contributed to the differences in epifaunal distributions observed. One possible explanation for the differences in abundance and size of epifaunal invertebrates near the platforms compared to far away is differences in food availability and predation. The authors mention that demersal fish were more abundant at the near-field station than at the far-field station at each platform. This probably is a reef effect: motile fish and invertebrates are attracted by the shelter and food (biofouling organisms) provided by the underwater platform structures (Bull and Kendall, 1994). The reef effect changes community structure and predator-prey relationships in a zone around each platform. Each platform will have a slightly different reef community, depending primarily on water depth and proximity to nearby natural reefs and topographic features. As discussed above, two of the platforms, MU-A85 and HI-389, are near natural banks and probably recruited reef/hard bottom fauna from these areas. The third platform is in shallow water and may have attracted fauna from coastal habitats.

Carr et al. (1996) determined the toxicity of sediment pore water in the vicinity of the 3 platforms in the GOOMEX study. The focus of the study was on HI-A389 where all waste discharges were shunted to within 10 m of the bottom, because sediments near this platform were the most heavily contaminated.

Some sediment samples collected near HI-A389 and MAI-868 were toxic in 1 or more of the sediment toxicity tests (Carr et al., 1996). None of the samples collected from MU-A85 was toxic. The most toxic sediments were collected within 150 m of HI-A389. There was a decrease in the number of toxic sediment samples between the first and second sampling cruises. This may have been caused by a heterogeneous distribution of toxic sediment components near the 2 platforms.

The best statistical correlation between toxicity and contaminant concentrations in sediment pore water was for lead. There also was a significant correlation between pore water toxicity and concentrations of zinc, mercury, and naphthalene. The platform exhibiting the highest level of sediment contamination and associated pore water toxicity (HI-A389) was a platform where drilling wastes were shunted to near the bottom. It is possible that some of the toxicity of sediments from near the platforms was caused by sulfide and ammonia, both of which are produced during microbial anaerobic biodegradation of organic matter, and were higher in near-field toxic sediments than in far-field sediments at HI-A389.

Even under these worst-case conditions with respect to near-field sediment contamination with water-base drilling muds and cuttings, apparent toxic effects in sediment organisms were restricted to a zone of less than 150 m from the platforms. Sediment toxicity could not be clearly attributed to concentrations of drilling waste-associated chemicals in sediments or to shunting of drilling wastes to the bottom. Half the sediments from the first survey and all the sediments from the second survey that were toxic at HI-A389 contained elevated concentrations of ammonia (Carr et al., 1996), suggesting that byproducts of organic enrichment could have contributed to the observed toxicity.

The studies discussed above as well as several others show that significant effects of drilling waste discharges on benthic ecosystems occur only when large amounts of solids accumulate on the bottom near the discharge site (shallow-water or shunted discharges to low-energy benthic environments) or the solids accumulations on the bottom (cuttings pile) contain a high concentration of biodegradable organic matter. Effects of cuttings piles on bottom living biological communities are caused mainly by burial and hypoxia caused by organic enrichment. Toxic effects, when they occur, probably are caused by sulfide and ammonia byproducts of organic enrichment, or by high concentrations of petroleum hydrocarbons (when OBM cuttings are discharged). Sediment petroleum hydrocarbon concentrations greater than about 50 to 60 mg/kg often are associated with altered benthic community diversity (Kingston, 1992). Ecological recovery of benthic communities from burial and organic enrichment occurs by recruitment of new colonists from planktonic larvae and immigration from adjacent undisturbed sediments. Recovery begins as soon as discharge of drilling wastes is completed and often is well advanced within a year. However, it may be delayed until concentrations of biodegradable organic matter decrease through microbial biodegradation to the point where surface layers of sediment become oxygenated (Hartely et al., 2003).

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7.0 APPENDICES

7.1 Glossary of Acronyms and Abbreviations Used in Review

APEO: Alkylphenol polyethoxylates; widely-used detergents. Degradation products, including nonylphenol and octylphenol are estrogen-disruptor toxicants.

API: American Petroleum Institute, Washington, DC

CAPP: Canadian Association of Petroleum Producers, Calgary, Alberta, Canada

CMC: Carboxymethyl cellulose; a viscosifier and fluid control agent for water based drilling muds

Eh: Reduction/oxidation (REDOX) potential, usually measured in millivolts or volts. An Eh below 0 usually indicates reducing (anoxic) water or sediment.

ELG: Effluent limitation guideline, developed by the U.S. Environmental Protection Agency, describes limitations on physical and chemical properties of liquid wastes destined for discharge to U.S. waters under a National Pollution Discharge Elimination System (NPDES) permit. ELGs are based on the degree of control that can be achieved using various levels of pollution control technology

EPA: U.S. Environmental Protection Agency

GC/FID: Gas chromatography with quantification by flame ionization detector

GESAMP: Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection is an advisory body of marine environmental experts that advises the sponsors (IMP, FAO, UNESCO-IOC, WHO, IAEA, UN, and UNEP) on prevention, reduction, and control of degradation of the marine environment.

GOOMEX: Gulf of Mexico Offshore Operations Monitoring Experiment, a 2-year monitoring program sponsored by the U.S. Dept. of the Interior, Minerals Management Service, to evaluate methods for monitoring long-term impacts of offshore production operations in the Gulf of Mexico on the marine environment

HEC: Hydroxyethyl cellulose; a viscosifier and fluid control agent for water based drilling muds

IO: Internal olefin; synthetic hydrocarbons used frequently in synthetic based drilling muds

LC/EC/IC₅₀: LC₅₀ – the median lethal concentration; the exposure concentration causing 50 % mortality; EC₅₀ – the median effects concentration; the exposure concentration causing a sublethal effect among 50 % of exposed organisms; IC₅₀ – the median concentration causing immobilization of test animals.

LAO: Linear- α -olefin; synthetic hydrocarbons used frequently in synthetic based drilling muds.

MMS: Minerals Management Service; a branch of the Dept. of the Interior, responsible for management of offshore minerals, including oil and gas, resources in U.S. federal waters

NADM: Non-aqueous drilling muds; drilling muds in which the continuous phase is not water. Included are oil based drilling muds (OBM) and synthetic based drilling muds (SBM), often called invert muds, in which the continuous phase is a refined petroleum product or a synthetic chemical, usually a hydrocarbon or ester.

NOEC: No observed effect concentration; the highest exposure concentration of a chemical at which no biological effects are observed

NPDES: National Pollutant Discharge Elimination System; Sections 402 and 403 of the Clean Water Act require that EPA issue National Pollutant Discharge Elimination System (NPDES) permits for discharges to the territorial seas, the contiguous zone, and the ocean that are in compliance with EPA's regulations for preventing unreasonable degradation of the receiving waters.

NSPS: New Source Performance Standards; operational standards included in NPDES permits for new discharges, based on best available technology

OBM: Oil based drilling mud; drilling mud in which the continuous phase is a refined petroleum product, usually diesel fuel, mineral oil, or a paraffin mixture.

OGP: International Association of Oil & Gas Producers, London, England

PAH: Polycyclic aromatic hydrocarbons, also called polynuclear aromatic hydrocarbons: hydrocarbons composed of 2 or more conjugated benzene rings. Most crude oils and distillate fuels contain a few percent PAH.

pH: Reciprocal of the hydrogen ion concentration in a liquid; a measure of the acid/base balance of a solution; a pH of 7 is neutral, lower values are acid, and higher values are alkaline.

PBM: Pseudo-oil based drilling mud; another name for synthetic based drilling muds (SBM), particularly those containing linear paraffins.

RPD: Redox potential discontinuity; the location in the water column or sediment where the reduction/oxidation (Redox) potential is 0 mV. Conditions are reducing below the RPD and oxidizing above it.

SBM: Synthetic based drilling mud; a drilling mud in which the continuous phase is a synthetic organic chemical, including synthetic hydrocarbons, ethers, esters, and acetals.

SPP: Suspended particulate phase; a drilling mud in water preparation required in the ELG for testing the toxicity of drilling muds to marine organisms. The suspended particulate phase is prepared by mixing 1 part drilling mud with 9 parts seawater, allowing the phases to separate, and using the aqueous phase (the SPP) for the test, usually with a mysid (a small shrimp-like crustacean)

TOC: Total organic carbon concentration; a measure of the concentration of organic matter in water or sediment

TPH: Total petroleum hydrocarbons; Usually measured by gravimetric, infrared, or gas chromatographic methods in water and sediments. The different analytical methods quantify different hydrocarbons and, therefore, give different results for TPH.

WBM: Water based drilling mud; a drilling mud in which the continuous phase is freshwater, seawater, or a saline brine.

7.2 Names of journals cited

Bull. Mar. Sci. – Bulletin of Marine Sciences

Can. J. Fish. Aquat. Sci. – Canadian Journal of Fisheries and Aquatic Sciences Chemosphere

Comp. Biochem. Physiol. – Comparative Biochemistry and Physiology

Contin. Shelf Res. – Continental Shelf Research

Deep-Sea Res. – Deep-Sea Research

Ecol. Model. – Ecological Modeling

Environ. Model. Software – Environmental Modeling and Software

Environ. Sci. Technol. – Environmental Science and Technology

Environ. Toxicol. Chem. – Environmental Toxicology and Chemistry

Environ. Pollut. – Environmental Pollution

Estuar. Cstl. Mar. Sci. – Estuarine and Coastal Marine Science

Fres. Environ. Bull. – Fresenius Environmental Bulletin

Fuel – Fuel

Geochem. Geophys. Geosyst. – Geochemistry, Geophysics and Geosystematics

Geochim. Cosmochim. Acta – Geochimica et Cosmochimica Acta

Geol. - Geology
Geomicrobiol. J. – Geomicrobiology Journal
Gulf Research Reports
ICES J. Mar. Sci. – ICES Journal of Marine Science
ICES J. Sea Res. – ICES Journal of Sea Research
J. Energy Res. Technol. – Journal of Energy Research and Technology
J. Environ. Monitor. – Journal of Environmental Monitoring
J. Environ. Qual. – Journal of Environmental Quality
J. Mar. Biol. Assn. U.K. – Journal of the Marine Biological Association of the UK
J. Petrol. Technol. – Journal of Petroleum Technology
Mar. Biol. – Marine Biology
Mar. Chem. – Marine Chemistry
Mar. Geol. – Marine Geology
Mar. Ecol. Prog. Ser. – Marine Ecology Progress Series
Mar. Environ. Res. – Marine Environ. Research
Mar. Pollut. Bull. – Marine Pollution Bulletin Nature, London
Oceanogr. Mar. Biol. Ann. Rev. – Oceanography and Marine Biology Annual Review
Oil & Gas J. – Oil and Gas Journal
Oil. Rev. – Oilfield Review
Phil. Trans. Roy. Soc. London – Philosophical Transactions of the Royal Society, London
SPE – Society of Petroleum Engineers
World Oil